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# In-Process Control of
# Nitrogen and Sulfur in
# Entrained-Bed Gasifers

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# IN-PROCESS CONTROL OF NITROGEN AND SULFUR IN ENTRAINED-BED GASIFIERS

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16. ABSTRACT The report gives results of an evaluation of theoretical aspects and engineering considerations of in-process pollutant control of the entrained-bed slagging coal gasification process, as applied to combined cycle operation or to the retrofit of existing boilers. The pollutants of concern are the nitrogen and sulfur oxides (NOx and SOx) which, without controls, are products of combustion of the gasifier product gas. A literature search and theoretical evaluation were conducted to identify the chemical/physical conditions and flow characteristics of entrained-bed slagging gasification as they relate to in-process control of NOx and SOx precursors. A tentative scheme was postulated to maximize the conversion of flue nitrogen species to elemental nitrogen by operating modifications and to remove H2S and HCN with the slag by injecting alkaline metal oxides into the gasifier gas space. However, the degree of success of the suggested in-process controls could not be projected. The applicability of potential in-process control was examined. It was concluded that in-process controls, if feasible, are applicable for reducing NOx and SOx precursors so that the capacities of downstream control devices can be reduced with subsequent cost savings.

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| Coal Gasification | Stationary Sources | 13H |
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# ABSTRACT

The objective of this project was to evaluate the theoretical aspects and engineering considerations for in-process pollutant control of the entrained bed slagging coal gasification process as applied to combined cycle operation or to the retrofit to existing boilers. The pollutants of concern were the nitrogen and sulfur oxides which, without controls, are products of combustion of the gasifier product gas. A literature search and theoretical evaluation was conducted to identify the chemical/physcial conditions and flow characteristics of entrained bed slagging gasification as they relate to in-process control of nitrogen and sulfur oxide precursors. A tentative scheme was postulated to maximize the conversion of fuel nitrogen species to elemental nitrogen by operating modifications and to remove $H_2S$ and HCN with the slag by injecting alkaline metal oxides into the gasifier gas space. However, the degree of success of the suggested in-process controls could not be projected.

The applicability of potential in-process control was examined. It was concluded that in-process controls, if feasible, are applicable for reducing $NO_x$ and $SO_x$ precursors so that the capacities of downstream control devices can be reduced with subsequent cost savings.

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## TABLE OF CONVERSION FACTORS

| To Convert From | To | Multiply by |
|---|---|---|
| Btu (thermochemical)/lb | joule per kilogram, J/kg | 2.324 444 E + 03[a] |
| million[c] Btu/hr | megajoule per hour, MJ/h | 1.054 350 E + 03 |
| Btu/scf[b] | joule per cubic meter, $J/m^3$ | 3.723 402 E + 04 |
| degree Fahrenheit, °F | kelvin (K) | $t_K = (t°_f + 459.67)/1.8$ |
| $ft^3/lb$ | cubic meters per kilogram, $m^3/kg$ | 6.242 796 E - 04 |
| grains/scf[b] | grams per standard cubic meters, $g/m^3$ | 2.288 352 E + 00 |
| lb/million Btu | kilogram per megajoule, Kg/mJ | 4.302 105 E - 04 |

[a] 2.324 444 E + 03 = $2.324444 \times 10^{+3}$

[b] scf, standard cubic feet = cubic feet at standard temperature (68°F = 20°C) and one atmosphere pressure [1.013 250 E + 05 pascal (Pa)].

[c] or $10^6$ Btu/hr.

# SUMMARY

The objective of this project was to evaluate the theoretical aspects and engineering considerations for in-process pollutant control of entrained-bed slagging coal gasification processes as applied to combined cycle operations or the retrofit of existing boilers. The pollutants of concern were the nitrogen and sulfur oxides which begin forming in the gasifier and are products of gasifier product gas combustion. Therefore, the goal of the study was to examine the potential for control within the boundaries of the gasification process to reduce or eliminate $NO_x$ and $SO_x$ precursors ($H_2S$, $NH_3$, HCN, etc.) that are formed in the gasifier. The target of such control is the elimination or reduction in scale of either downstream cleanup devices or combustion stack gas cleanup controls, or both.

The project, which commenced in February 1985 and was completed in September 1986, consisted of two phases or tasks:

Task 1 Theoretical Evaluation: Literature search and theoretical evaluation in regard to in-process control.

Task 2 Applicability: Assessment of the effects of in-process control on gasification product gas streams and the associated impact on the downstream processes.

The objective of Task 1 was to evaluate the information available concerning chemical/physical conditions and flow characteristics of atmospheric and pressurized, high temperature, slagging gasification as related to in-process control of $NO_x$/$SO_x$ precursors. The task was divided into five general areas:

1. literature search and the gathering of information pertinent to entrained-bed slagging gasifiers and possible in-process controls,

2. control theory and experience for $SO_x$ and $NO_x$ and their precursors,

3. gasifier in-process conversions of nitrogen and sulfur compounds in light of a combined effort to control both $SO_x$ and $NO_x$ precursors,

4. developing the concept of a model for defining operating modes that optimize in-process control for $SO_x$ and $NO_x$ precursors, and

5. examining the applicability of the potential in-process controls for reducing or eliminating downstream pollution controls.

The results are based on an intensive literature review and close examination of the most applicable work that has been done in the areas of concern. A combination of in-process control schemes offering the most promise includes:

- staged injection of the oxidant for $NO_x$ and $NO_x$ precursor control,
- staged injection of an alkaline capture material for $NO_x/SO_x$ precursor control, and
- manipulation of the gasifier operating variables for $NO_x/SO_x$ precursor control.

The evaluations were restricted to a fairly narrow definition of "in-process control," including only the gasification and quench zones. Nevertheless, some flexibility was allowed in cases where conditions for a given reaction to occur were only marginally within the gasification and quench regimes. This approach is reasonable because much of the work reported in the literature is theoretical or based on limited experimental confirmation. Some control techniques, such as hot gas cleanup and thermal de$NO_x$, might also be considered in the marginal category. Their applicability to entrained-bed slagging gasification will be examined in Task 2. Task 1 results and conclusions are summarized as follows.

## Information Resources

The literature was searched in three primary areas:

1. entrained-bed slagging gasifiers,
2. In-process controls for entrained-bed slagging gasifers,
3. nitrogen and sulfur species reaction mechanisms at gasifier conditions and theoretical models encompassing these reactions.

The search for in-process controls did not produce substantial information or data. However, a body of information for other gasification processes and LIMB technology was of some use. Considerable work has been done to establish an understanding of nitrogen and sulfur species reaction mechanisms. These data are summarized below (Control Theory and Experience).

Theoretical models that include the optimization of nitrogen and sulfur species control were not available, but entrained-bed gasifier models have been developed that could be revised to accept the nitrogen and sulfur species control kinetic and thermodynamic data.

Information about entrained-bed slagging processes that are under development or commercialized was collected to define the chemical, physical, and flow conditions. Five processes (KBW, Saarberg-Otto, Shell, Texaco, and TRW) were selected to provide an approximate range of base case characteristics within which gasifier operation can be varied to achieve effective in-process control. Major syngas characteristics that are important for application to the two end uses, combined cycle or retrofit, are:

- pollutant levels,
- pressure levels,
- gas heating value, and
- active component ratio ($CO/H_2$).

Emission limitations for $NO_x/SO_x$ define precursor levels which must be attained to eliminate downstream controls; particle loading of the gasifier exit gas must be controlled to protect the gas turbine. Pressure level choice, atmospheric or elevated, depends on the application and on optimum design of the overall gasification/combustion system. Thus, either atmospheric or pressurized operation is considered applicable. All other things being equal, medium-Btu gas is favored over low-Btu gas for the applications considered. However, economics may dictate the use of low-Btu gas in some cases due to the high cost of oxygen production. For the combined cycle end use, maximum $CO/H_2$ ratio is desirable for providing maximum mass to the gas turbine if it is consistent with the overall energy balance.

If oxidant staging, injection of a capture material and its staging, and manipulation of operating variables are to be the gasifier in-process controls for $NO_x/SO_x$ precursors, then the assumption is that specific operating conditions will play a dominant role in optimization of in-process control. The prominent control variables in the gasifier and the operating conditions which influence these variables are:

- oxidant staging: dependent on burner design,

- temperature: dependent on oxygen/coal ratio, steam/coal ratio, oxidant, feed stream temperatures, coal composition and heat losses,

- residence time in the gasifier/slagging zone: dependent on reactor volume, gasification temperature, coal particle size, and flow rates for coal, steam, and oxidant, and

- temperature zones (gasifier and cooling): dependent on reactor design (volume reactor geometry, wet or dry cooling, slag removal).

These gasifier operation and design considerations as they relate to possible in-process controls were examined. The tentative conclusions regarding the flexibility of gasification processes for the application of in-process controls are summarized as follows:

- Compatibility of oxidant feed for in-process controls with base case oxidant feed methods will need to be determined. At least one process employs staged oxidant feed for $NO_x$ control.

- There is some latitude in manipulation of $O_2$/coal and steam/coal ratios if needed for in-process control.

- There is considerable latitude in how much the $CO/H_2$ ratios can be varied and still produce an acceptable product gas.

- Compatibility of residence times and temperatures required for optimum in-process controls with base case residence times will need to be determined.

- Two temperature zones within the gasifier provide an opportunity for staged injection of capture materials that will avoid or minimize sintering.

The literature was searched for pollutant levels at the exit of the gasifier that can be used as base cases from which $NO_x/SO_x$ precursor concentrations can be lowered by in-process control. Reports of pollutant species concentrations before particulate matter and ammonia scrubbing are sparse. Therefore, a base case untreated gas composition was pieced together from several design and actual operation sources; this composition is believed to represent a base case reasonably well.

## Control Theory and Experience

The reactions which take place in an entrained-bed gasifier can be grouped into the following general categories: coal devolatilization, combustion of volatiles, combustion and gasification of resulting char, homogeneous oxidation of carbon monoxide and hydrogen, and the steam reforming of methane. Of these, only reactions in the first three categories play a significant role in the generation and fate of nitrogen and sulfur species in the gasifier. Studies at gasifier conditions are usually carried out for either nitrogen or sulfur species, but not both. Therefore, as an initial step we had to examine the reactions separately.

Devolatilization of the coal takes place rapidly at gasifier temperature to form char and a gas fraction consisting primarily of CO, $H_2$, $CO_2$ and $CH_4$. Significant quantities of HCN and $NH_3$ are also often reported. The quantity of volatiles produced has been shown to be a function of several factors as summarized below:

- Volatiles yield generally increases as particle size decreases.
- Changes in particle heating rate in the range of 600 to 50,000°C/sec produce very little effect on volatiles yield.
- Devolatilization at elevated pressure retards the escape of gaseous species and hence volatiles yield.
- Coal type is an important variable. One investigator found yields from Pittsburgh seam bituminous coal to increase with decreasing particle size and decreasing pressure, while yields from Montana lignite were independent of both pressure and particle size.

The results of one study of fuel-rich coal combustion indicated that 50 to 60 percent of the original coal nitrogen remained in the char. Both total and nitrogen volatiles increased at higher oxygen stoichiometries probably due to higher pyrolysis temperatures resulting from increased combustion rates. Total and nitrogen volatile yields will likely be lower under pressure gasification conditions (e.g., higher pressure and lower temperature).

Most workers in the field generally believe that HCN is the primary nitrogeneous intermediate formed during pyrolysis of fuel nitrogen compounds. Subsequently, HCN reacts with other gaseous species to form $NH_3$, NO, and $N_2$.

The literature indicates that some combustion of volatiles occurs according to the amount of oxygen available. For the nitrogen case, the results suggest that HCN and other fixed nitrogen species are oxidized quickly to NO shortly after devolatilization. As the gas becomes fuel-rich due to gasification of the char, NO is reduced to $N_2$.

The nitrogen which is not devolatilized during pyrolysis is consumed during combustion and gasification of the resulting char. If sufficient oxygen is available, char nitrogen will oxidize to form NO. More likely, oxygen will be depleted by combustion of volatiles and carbon and char nitrogen will evolve as HCN. In either case, the gaseous nitrogen species will combine with other gaseous species and react according to mechanisms that occur during the combustion of volatiles.

Since both HCN and $NH_3$ in gasifier exit gas will be converted to $NO_x$ by subsequent combustion of that gas, the objective of in-process control in the gasifier is to convert a maximum fraction of fuel nitrogen to $N_2$. A number of studies have been conducted involving fuel-rich combustion of coal in which these same phenomena have been examined. The results of these studies can be applied to entrained bed gasifiers to suggest trends which might result from changes in process and operating variables.

Based on these results, the following process parameter changes are suggested as a means to increase the conversion of fuel nitrogen to $N_2$ in an entrained-bed gasifier:

- operate at higher $O_2$/coal ratios and hence higher temperatures
- decrease the particle size of feed coal,
- inject a small amount of oxygen 50 to 100 msec downstream of flame zone in the gasifier, and
- inject small amounts of alkaline metal oxides (e.g., lime) at several points 50 to 5,000 msec downstream of flame zone in the gasifier.

The results were gathered at atmospheric pressure. With the exception of the impact of pressure on devolatilization (whose effect is coal-specific), the results at atmospheric pressure are expected to be similar to those at elevated pressures.

Under normal entrained-bed gasifier conditions, 85 to 90 percent of the fuel nitrogen which enters the gasifier is converted to $N_2$; the remainder exits as $NH_3$ and HCN. The objective of the process changes described above would be to raise the convertion to $N_2$ to 95 percent or greater in order to combust the fuel gas in a new gas turbine and meet NSPS limitations without additional $NO_x$ control techniques. It is not possible, at this time, to project the $N_2$ conversion that would result from the recommended changes due to the complex interactions of process parameters and their effect on gas composition. A validated process model and/or experimental data collected under representative conditions would be most useful in this regard.

For the sulfur species case, as with nitrogen coal devolatilization, combustion of volatiles and combustion and gasification of the resulting char also play a dominant role in identifying the fate of coal sulfur. Sulfur is present in coal in three forms: organic sulfur, inorganic sulfur, and elemental sulfur. Review of work on the kinetic and thermodynamic relationships affecting sulfur species reactions at high temperatures reveals the following major expected effects:

- Pyrolysis of coal in the fuel-rich reducing atmosphere leads to devolatilization of sulfur compounds which readily are reduced to produce $H_2S$ through the hydrodesulfurization mechanism. The reaction rate is very fast.

- COS and $CS_2$ are formed in the gasifier due to the reactions of devolatilized sulfur in the gas phase with carbon and the reaction of $H_2S$ with $CO_2$. COS is detected in gasifier effluents in small amounts but $CS_2$ is usually not reported.

- Some of the $H_2S$ is expected to react with the available basic oxides of the ash and thus be retained in the slag.

It appears, then, that if sulfur capture materials are to be injected they need to be materials that will react with or adsorb the $H_2S$ in the gas phase. Surprisingly, $SO_2$ has been detected in the gas phase of an entrained-bed gasifier at a point before complete burnoff of the char.

Considerable information on the reactions of CaO with $H_2S$ and $SO_2$ is available from LIMB and other experimental studies. The principal variables that determine the rate of capture are temperature, specific surface area of the lime, and $H_2S$ and $SO_2$ partial pressures. A negative temperature dependence is indicated. Also, temperatures in excess of 1000°C introduce significant surface area loss as a result of sintering. Other sorbents may have greater resistance to sintering. Copper oxide has been used in a fluidized bed for sulfur and nitrogen species control. High temperature desulfurization/regeneration reactions involving several metal oxides and carbonates have also been studied. Sources of alkaline material other than CaO are suggested. Two readily available waste materials, cement kiln dust and alkaline fly ash, are offered as potential capture materials. Tricalcium silicate, a component of Portland Cement, has demonstrated 60 percent $H_2S$ capture at 1000°C. There is an apparent negative dependence on temperature above that temperature. The rate of sulfidation is affected by $CO_2$ content in the gas phase.

The use of metal oxides other than calcium as desulfurization media has been examined by the Morgantown Energy Research Center (MERC) for possible application as a hot gas contaminant control in the gasifier product stream. In addition, several investigators have reported on the thermodynamic equilibrium and kinetic studies pertaining to reactions for the sulfidation of metal oxides by $H_2S$ that, while not directly applicable to in-process control, may be useful for rational extrapolation. Most metals can be eliminated from consideration on the basis of thermal instability in the gasifier temperature range, undesirable side reactions, unfavorable kinetics, or gas phase products that preclude removal with the slag. On the basis of thermodynamic studies there are indications that the oxides of barium and strontium (and perhaps manganese) have potential as in-process sorbents. Of the candidate metal oxides, the reaction rate for the sulfidation of MnO is exceeded only by $Fe_2O_3$ in the gasifier temperature regime. However, MnO sulfidation is accompanied by undesirable side reactions. Thermodynamic analyses do not address the physical phenomena, such as desurfacing, which may occur to solid sorbents at high temperature and little information was found on physical effects work for metal oxides other than CaO.

## Combined Effort for Control of $NO_x$ and $SO_x$ Precursors

The preceding discussion has suggested manipulation of operating conditions and staged oxidant injection for $NO_x$ precursor control and injection of a stable alkaline material for $SO_x$ precursor control. The literature appears to address either the issue of $SO_x$ control or $NO_x$ control. Very few attempts to consider the effect of alkali oxides on gasifier intermediates such as HCN have been noted.

If CaO is added to the gasifier, competing reactions between CaO and HCN would significantly affect the concentration of HCN. If a portion of the HCN normally found is effectively removed from the gasifier reaction mix by complexing with CaO, the amount of $NH_3$, NO, and $N_2$ subsequently formed will also be reduced. The concentration of these final nitrogen products exiting the gasifier would be reduced in roughly the same proportion as the amount of HCN complexed by CaO. For example, if the exit gas from a gasifier contained 6000 ppm $N_2$, 2000 ppm $NH_3$, and 300 ppm HCN under normal operating conditions, and CaO were added to the gasifier and reacted with one-half of the HCN produced during devolatilization, the new exit gas would be expected to contain approximately 3000 ppm $N_2$, 1000 ppm $NH_3$, and 150 ppm HCN.

Acidic HCN and basic CaO are expected to undergo a neutralization reaction that results in calcium cyanamide (CaNCN) as the reaction product. One would expect that the rate of absorption of HCN with CaO will parallel the rate of absorption of $H_2S$ by CaO since both HCN and $H_2S$ are acidic gases. During the absorption of $H_2S$ by lime, the rate of reaction is found to be dependent on the reaction temperature and the desurfacing of CaO. Surface activity is dependent on temperature and plays an important role in the absorption of the acid gas. Probably such a phenomenon is important in the CaO + HCN reaction also.

It is expected that the sulfur and nitrogen compounds captured by the added calcium oxide will be removed from the reactor with the slag. For $H_2S$ absorption, the rate limiting step appears to be the internal particle diffusion process. Although diffusion itself is not a strongly temperature-dependent phenomenon, desurfacing is rapid at usual gasifier temperatures and will have a dramatic effect on reducing the $H_2S$ absorption rate on CaO. Experimental observations suggest that CaO should be added to the gasifier at lower temperatures. The coal conversion requirements for an efficient gasifier demand that it be operated at higher temperatures. A possible compromise for maximum absorption activity and minimum desurfacing activity for lime may be to add lime in the regions of lower temperature away from the flame. Probably a staged addition of lime will have to be adopted to facilitate removal of $NO_x$ and $SO_x$ precursors. Part of the CaO may be added with the coal slurry to capture $H_2S$/HCN released in the initial devolatilization, whereas the major portion of the lime may be added in the temperature regions of 800 to 1000°C. These temperatures correspond to the cooling zone of the gasifier.

## Model Concept Development

In the preceding discussion we have indicated potential means of reducing $NO_x/SO_x$ precursor concentrations through in-process control. Without an available theoretical model that has been validated with actual results, the specific effects on product gas quality and precursor concentrations could not be projected. The utility of a theoretical model is to be able to calculate what the exit conditions are over a range of gasifier operating conditions and to be able to determine operating conditions which minimize exit concentrations of the pollutant precursors. The literature surveyed revealed that several models exist for entrained-bed slagging gasifiers. However, none of these models applies to control of nitrogen and sulfur species in the gasifier.

An investigation was made into the feasibility of adopting an existing model for the prediction of nitrogen and sulfur species control effects. A model that was verified from Texaco pilot plant data was chosen. It was concluded that this model could be adopted as needed. Added assumptions would need to be made about the reaction surface area of CaO. The voidage fraction of CaO particles would need to be reduced from any measured values at ambient temperature to account for sintering at temperatures to be found in the entrained-bed gasifier.

## Applicability of In-Process Controls to Utility and Industrial Situations

A further objective of this study was to examine the effects on utility and industrial users of providing a cleaner fuel gas by means of in-process gasifier controls. In particular, the effects on new combined cycle plants and on retrofit utility and industrial boilers were investigated. In preceding sections it was reported that although in-process controls show promise for reducing $NO_x/SO_x$ emissions, it does not appear that these pollutants can be completely eliminated. Therefore, the applicability of in-process modifications is limited to reducing the capacity but not completely eliminating downstream controls. The applicability of in-process controls was also examined in relation to fuel specifications for gas turbines and to emission limits of all of the potential users.

Reducing the concentration of the reduced nitrogen species is a major advantage obtained from in-process controls. Thermal $NO_x$ formation during combustion will occur in proportion to elemental nitrogen in the fuel and in the combustion air. Tests have shown that the fuel $NO_x$ contribution of entrained-bed gasifier product gases is well within industrial and utility emission limitations for $NO_x$ without in-process controls. Therefore, in-process control is primarily applicable for capacity reduction of downstream $NO_x$ controls.

Gasifier downstream controls that are located ahead of the combustion device are directed primarily at reducing the amount of particulate matter and sulfur species. One exception is the removal of $NH_3$ by water scrubbing for $NO_x$ control. Scrubbing processes for the removal of $NH_3$ and $H_2S$ result in a lower temperature of the gas that is fed to a gas turbine in a combined cycle operation. The NSPS emission limits for total $NO_x$ (fuel $NO_x$ and thermal $NO_x$) from electric utility gas turbines are about one-half the emissions projected from medium-Btu gas and only slightly lower than the emissions projected from low-Btu gas. It appears, then, that a modest reduction in gasifier $NH_3$ and HCN emissions by in-process controls would result in compliance with NSPS for $NO_x$ emissions from low-Btu gas-fed turbines. It would perhaps also eliminate the need for the downstream ammonia scrubber. However, medium-Btu gas would require in excess of 50 percent reduction of nitrogen species from the gasifier because thermal $NO_x$ is a significant contributor to total $NO_x$ emissions when medium-Btu gas is the fuel. Therefore, it is likely that $NH_3$ scrubbing or hot gas cleanup would still be required with in-process controls for gas turbine applications.

Assuming current and proposed $SO_2$ emission limitations for boilers that are based on heat input to the coal gasifier, it can be shown that gasifiers without in-process controls require substantial control device capacity either downstream of the gasifier or of the boiler. Removal efficiency requirements will vary depending on industrial- or utility-boiler applications, on air-blown (producing low-Btu gas) or oxygen-blown (producing medium-Btu gas) operation, or on coal sulfur content. In-process controls would limit control device capacity requirements. For example, if the coal feed to the gasifier contains 3.5 weight percent sulfur and has a heating value of 12,000 Btu/lb,* the utility boiler NSPS would require 89.7 percent $SO_2$ removal to meet an emissions limit of 0.6 lb $SO_2$/million Btu. If in-process controls are applied that reduce $SO_2$ precursors by 50 percent, $SO_2$ removal requirements would be reduced to 79.3 percent, thus reducing the size and cost of a downstream control device.

For the gas turbine application, sulfur species concentrations are restricted by NSPS limits for sulfur in the fuel gas, $SO_2$ emissions in the gas turbine exhaust, and turbine design specifications to limit turbine blade corrosion. It appears unlikely that in-process controls for sulfur species can achieve the level of sulfur control required. Therefore, as with boiler applications, the primary benefit would be a reduction of the burden on downstream control devices.

Particulate matter (PM) control of gasifier product gas for gas turbine and boiler applications is substantially influenced by design specifications. For the gas turbine, PM loadings down to 0.001 grain/scf are required to avoid turbine blade erosion. For boilers, PM concentration in the fuel gas must be limited to nearly the same order of magnitude to protect the gas furnace from erosion and plugging. These design restrictions mandate that PM controls precede combustion. The use of dry sorbent injection for in-process sulfur control will increase the PM loading of the gasifier product, putting further demands on PM control devices.

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* Readers more familiar with the metric system may use the conversion table on p. x of this report.

# 1.0 INTRODUCTION

## 1.1 OBJECTIVE

The objective of this project was to evaluate the theoretical aspects and engineering considerations for in-process control of sulfur and nitrogen pollutants from entrained-bed slagging coal gasification processes used to fuel utility power plants and industrial boilers and to supply combined cycle power plants. The project commenced in February 1985 and was completed in September 1986.

## 1.2 BACKGROUND

Considerable effort has been and is being directed toward the development of entrained-bed slagging coal gasifiers for commercial use. The entrained-bed slagging gasifier process has a number of applications including, among others, (1) as a coal gasification process that provides fuel and thermal energy for combined cycle power plants, and (2) as a precombustor to replace conventional coal, oil, or gas firing of utility or industrial boilers. At least one combined cycle plant employing entrained-bed slagging gasification (Cool Water Coal Gasification Program) is operating. In addition, extensive development work is underway on entrained-flow slagging coal combustors, focusing on retrofit applications for coal-, oil-, and gas-fired boilers.

The principal pollutants emitted from a gasifier are $NH_3$, $H_2S$ and particulate matter with lesser amounts of NO, HCN, COS and $CS_2$. Typically, gasification processes rely on downstream pollution controls for the control of the precursors of $NO_x$ and $SO_x$ and of particulate matter. Downstream control systems usually include a physical solvent process for $H_2S$ removal and aqueous scrubbers for $NH_3$ and particulate matter removal.

Entrained-bed gasification operating conditions in the fuel rich zone closely parallel conditions that have been found conducive to staged combustion $NO_x$ control. Additionally, the process has potential for in-process control of $SO_x$ precursors by injection of sulfur capture materials and subsequent removal in the slag. Accordingly, AEERL, through its Advanced Processes Branch, has an interest in expanding what is known about the potential for in-process nitrogen and sulfur control for entrained-bed coal gasification. The ultimate goal is the reduction or elimination of $NO_x$ and $SO_x$ precursors ($H_2S$, $NH_3$, HCN, etc.) that are formed in the gasifier. Of particular interest are in-process pollutant control schemes for gasifiers that are a part of new combined cycle plants (where fuel gas is burned in a gas turbine) or are retrofits to existing gas- or oil-fired boilers. The target for such effort is the elimination or reduction in scale of downstream cleanup devices. A simplified process flow diagram which illustrates this concept is presented in Figure 1-1.

As a result, AEERL initiated this study to evaluate the potential for in-process nitrogen and sulfur control and its applicability to coal gasification plants that feed new combined cycle plants or that are retrofitted to existing coal-, oil-, or gas-fired boilers. In-process control includes both manipulation of gasifier operating conditions and design variables and the addition of supplemental materials to reduce the concentration of $NO_x$ and $SO_2$ precursors. The major equipment pieces included in the boundaries of in-process control concepts are the gasifier and heat recovery vessels used for gas cooling.

## 1.3 APPROACH

The scope of this program is restricted to a paper study using readily available information. The project was divided into two phases or tasks:

Task 1 Theoretical Evaluation: Literature search and theoretical evaluation of potential for in-process control.

Task 2 Applicability: Assessment of the effects of in-process control on the profile of gasification product gas streams and the associated impact on downstream processes.

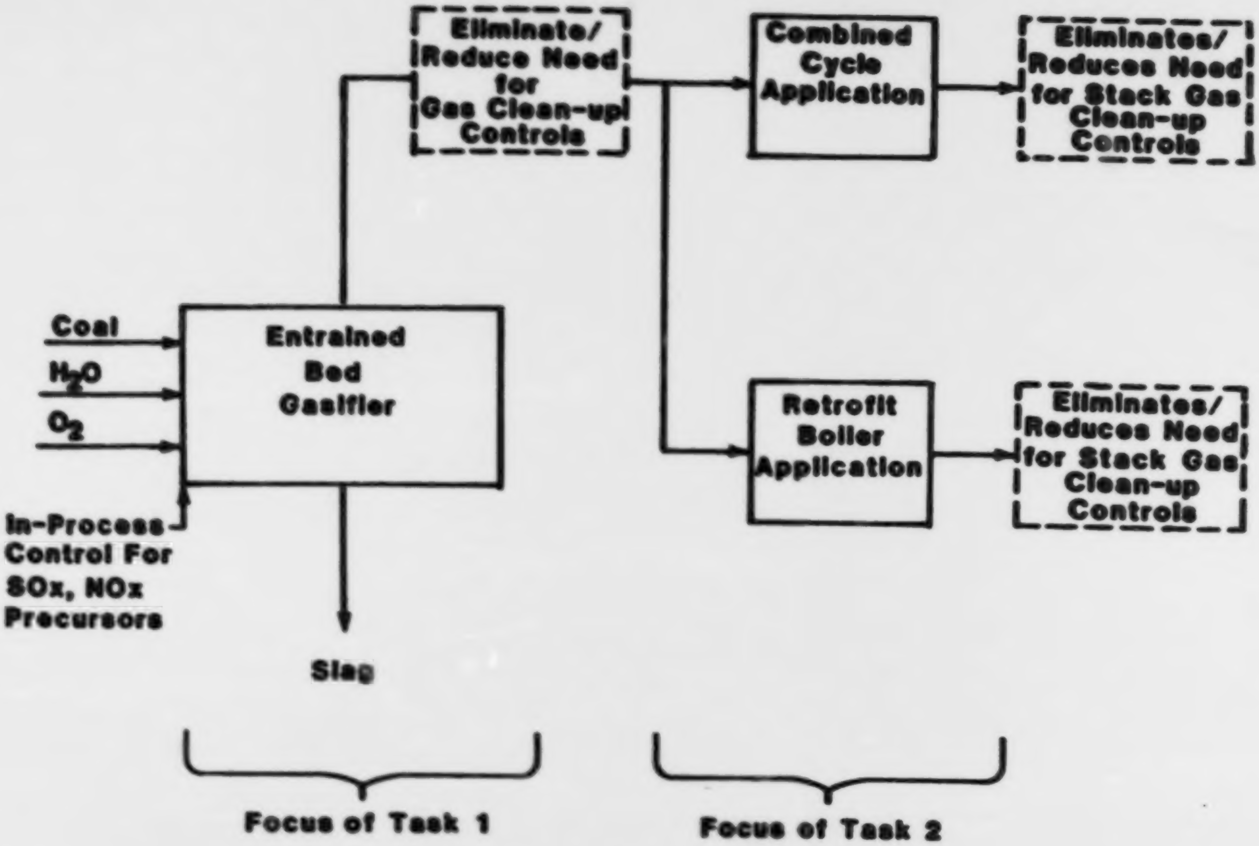
Eliminate/ Reduce Need for Gas Clean-up Controls
Combined Cycle Application
Eliminates/ Reduces Need for Stack Gas Clean-up Controls
Coal
$H_2O$
$O_2$
Entrained Bed Gasifier
In-Process Control For SOx, NOx Precursors
Retrofit Boiler Application
Eliminates/ Reduces Need for Stack Gas Clean-up Controls
Slag
Focus of Task 1
Focus of Task 2

Figure 1-1. Entrained-bed gasifier in-process control concept.

The work for this project was performed in 1985. The literature through about January 1985 was surveyed to obtain background information for the tasks described.

## 1.4 REPORT ORGANIZATION

This report is organized as follows: Section Two describes five entrained-bed slagging gasifiers that are under development or commercialized. This information provides the base cases from which pollutant control modifications can be considered. Sections Three and Four present analyses of mechanisms for $NO_x$ and $SO_x$ control, respectively. Section Five restates these principles in light of simultaneous in-process control of $NO_x$ and $SO_x$ precursors. Section Six presents a basic framework for modeling the nitrogen and sulfur reaction mechanisms in the gasifier regime. Section Seven gives general information on gas turbine design and operation including details on gas turbine emissions, available control techniques. It also covers potential impacts of firing gasifier product gases in gas turbines. Section Eight examines the implications of using gaseous products from an entrained-bed gasifier, with and without in-process controls, as a fuel for new boiler installations or for retrofit use on existing utility and industrial boilers.

## 2.0 GASIFICATION PROCESSES

There are several entrained-bed slagging gasifier processes which are either currently under development or have reached the commercialization stage. Some promising processes for supplying gas to combined cycle plants or to existing boilers are Texaco, Shell, KBW, TRW, Koppers-Totzek, and Saarberg-Otto. The scope of this study includes only two downstream uses of the syngas: as feed to new combined cycle power plants or to oil- and gas-fired boilers that have been retrofitted for syngas firing. The above-mentioned gasification processes are examples of processes capable of producing gas for at least one of the two end uses. Therefore, they provide the base case characteristics of gasification processes to consider in an evaluation of in-process pollutant control. In this section we shall define these base case characteristics and their ranges within which gasifier operation can be varied to achieve effective in-process control. The major elements of gasification process characteristics that will be examined are:

- the product gas profiles for the two end use requirements,
- typical downstream controls,
- gasifier design and operation, and
- typical untreated gas compositions.

### 2.1 PRODUCT GAS PROFILES

The major syngas characteristics that are important for application to the two end uses are:

- pollutant levels,
- pressure levels,
- gas heating value, and
- active component composition ($CO + H_2$).

The impacts of each of these factors on end use requirements are discussed below.

(a) For the combined cycle application, $NO_x$ and $SO_x$ precursors are at present controlled with pre-combustion controls. The gas must also be essentially particle free to protect turbine internals. For the boiler retrofit base case, either pre-combustion or post-combustion pollution controls could be employed. To avoid either pre-combustion or post-combustion downstream controls, in-process controls need to limit $NO_x$ and $SO_x$ precursors in the raw synthesis gas to allowable emission levels. Current New Source Performance Standards (NSPS) restrictions, in place or proposed, are summarized in Table 2-1. "Raw gas" is defined for this study as gas emitted directly from the gasifier before any treatment for removal of $NO_x/SO_x$ precursors. The subject of particulate matter control was not addressed in Task 1; this subject will be considered in Task 2.

(b) Syngas at elevated pressure is typical for combined cycle operation, although some designs with atmospheric gasifiers have been considered.[1] Actual gasifier pressure depends on the optimum level for gasifier operation and the optimum level for gas turbine efficiency and overall heat balance. Elevated pressures range from 400 psi to 600 psi for the pressure gasification processes examined. Optimum pressure for the boiler retrofit end use depends on the characteristics of individual boilers. For example, minimum modification to the burner feed system would be required if the gasifier pressure matched the existing natural gas supply pressure.

(c) Maximum heating value of the product gas, accomplished by minimizing inerts ($CO_2$, $N_2$), is desirable for both applications. Retrofit of an air-blown gasifier producing low-Btu gas to existing gas- or oil-fired boilers may require extensive duct and fan modifications to handle the additional flue gas.[2] These same considerations will apply to a new

## TABLE 2-1. $NO_x$ AND $SO_2$ NEW SOURCE PERFORMANCE STANDARDS FOR COAL-FIRED GAS TURBINES AND BOILERS

| | Utility System | Industrial System |
|---|---|---|
| Gas Turbine $NO_x$: | 75 ppm[b] ($\sim$0.28 lb/$10^6$ Btu) | Same as utility systems |
| Gas Turbine $SO_2$: | None proposed | Same as utility systems |
| Boiler $NO_x$: | 0.7 lb/$10^6$ Btu - PC boiler | 0.7 lb/$10^6$ Btu - PC boiler[c]<br>0.6 lb/$10^6$ Btu - Spreader stoker[c]<br>0.5 lb/$10^6$ Btu - Mass feed stoker[c] |
| Boiler $SO_2$: | 70-90 Percent reduction sliding scale with 1.2 lb/$10^6$ Btu ceiling and 0.6 lb/$10^6$ Btu floor. | 1.2 lb/$10^6$ Btu[a] |

[a] For units above 250 million Btu/hr heat input.

[b] For units greater than 9 $MW_e$ output; 150 ppm for units between 1 and 9 $MW_e$ output; no NSPS below 1 $MW_e$ output.

[c] For units above 100 million Btu/hr heat input.

boiler burning low-Btu gas. On the other hand, the high cost of producing oxygen has to be factored in when considering oxygen-blown operation compared to the air blown option.[3] Typical gas heating values for oxygen-blown operation are around 300 Btu/scf while those for air-blown operation are closer to 150 Btu/scf.

(d) Maximum $CO/H_2$ ratios, consistent with the overall energy balance of the entire system, are desirable for providing maximum mass to a gas turbine. Active component composition is less important to the boiler retrofit case. Typical $CO/H_2$ ratios of the processes examined range from 1.0 to 2.5.[3-9]

## 2.2 BASE CASE DOWNSTREAM CONTROLS

Typical gasification/combustion concepts employ pre-combustion downstream controls to remove particulate matter, ammonia and $H_2S$. Also, steam is usually injected into gas turbine combustors to control $NO_x$ formation. It is the purpose of this task to examine possible gasifier in-process alternatives to the downstream $NO_x/SO_x$ controls employed at present.

Typically, the following gas conditioning steps take place downstream of the gasifier:

- gas cooling by convective heat exchange and direct water quench,
- gas scrubbing or dry collection to remove particulate matter,
- gas scrubbing to remove ammonia,
- gas treatment to remove $H_2S$, COS, and possibly HCN, and
- recovery of sulfur components as sulfur followed by tail gas cleanup.

The pre-combustion control methods described in the rest of this section have been identified with specific gasification processes but are nevertheless applicable to almost any process.

### 2.2.1 Particulate Matter Controls[4,10]

After gas cooling and saturation, Texaco and Shell scrub the raw gas to remove particles. KBW uses a series of steps: a hot cyclone, a disintegrator and an electrostatic precipitator. Saarberg/Otto employs a hot cyclone followed, after gas cooling, by a fabric filter. The TRW slagging combustor has no controls, since the gasifier stage is flanged directly to a combustor. Although the elimination or reduction of downstream particulate matter controls is desirable, the primary focus of this task is on $NO_x/SO_x$ precursor control and not on particulate matter control.

### 2.2.2 Ammonia Control[3-9]

Texaco and Shell absorb ammonia in water at about 40°C and elevated pressure. Ultimately, the water is stripped to remove ammonia and other components before discharge of the waste water. Gas overhead from the stripper may be fed to a sulfur recovery unit, combusted, or sent to $NH_3$ recovery. Texaco can recycle ammonia rich condensate, along with other ash/carbon containing streams, to the gasifier coal slurry feed stream. Ammonia control by KBW and Saarberg/Otto are not reported. Again, TRW has no precombustor controls.

### 2.2.3 Acid Gas ($H_2S$) Control[4,5]

In the references we examined, Texaco and Shell employed the Selexol process, a physical absorption method that uses the dimethylether of polyethylene glycol as the solvent. The solvent has an affinity for $H_2S$, COS, $CO_2$ and mercaptans but it can be operated to achieve selective absorption of the sulfur gases. The solvent is regenerated with steam or inert gases. The reported $H_2S$ removal process for Saarberg/Otto is by treatment with ferric hydroxide to form ferric sulfide:

$$2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O \tag{2-1}$$

It is reported that cyanides are also removed by this method.[5]

Generally, sulfur removal technologies can be fitted to any of the gasification processes. Other acid gas removal processes similar to Selexol are available that result in a $H_2S$ rich gas stream that can be further treated to recover the sulfur. The removal processes include amine treatment, Stretford, and Rectisol, another physical absorption method using methanol as the solvent.

### 2.2.4 Sulfur Recovery[5]

Sulfur can be removed by a number of processes, e.g., Stretford and Claus. The Claus process is a catalytic process that converts stoichiometric amounts of $H_2S$ and $SO_2$ to elemental sulfur and water. The reaction is limited by chemical equilibrium and, therefore, sulfur compounds are present in the tail gas.

### 2.2.5 Tail Gas Treatment[5]

The Beavon-Stretford and the SCOT processes have been reported for this application. Beavon-Stretford catalytically converts all sulfur compounds to $H_2S$ which is then oxidized to elemental sulfur in an oxidizing alkaline solution. The SCOT process, as with Beavon-Stretford, catalytically hydrogenates all sulfur compounds to $H_2S$. The $H_2S$ is then absorbed in an amine solution and the stripped $H_2S$ is recycled to the Claus plant.

## 2.3 GASIFIER DESIGN AND OPERATION

In order to develop in-process control theory for $NO_x/SO_x$ precursors, it is necessary to understand the possible reactions of nitrogen and sulfur species within the gasifier. These species are not limited to those that are observed in the exit raw gas stream. They also include those that are formed as intermediates in the gasifier and which subsequently undergo further reactions to produce the final raw gas exit composition. The conditions that are expected to affect in-process nitrogen and sulfur controls are summarized in Table 2-2. The control variables on the left side of Table 2-2 have been selected as those most affecting control of $NO_x$ and $SO_x$ precursors. The connection between these control variables and $NO_x/SO_x$ precursor controls will become apparent as the entrained-bed slagging gasifier is described.

Table 2-3 summarizes some process information for five processes mentioned above. Coal, oxidant, and steam are fed so as to obtain rapid devolatilization and char burnoff in a relatively small gasifier volume. Opposed burner, offset burner, and swirling burners may be used to accomplish rapid temperature buildup and fast reaction. If oxidant staging is a strategy for increasing the conversion of fixed nitrogen species to $N_2$ in the gasifier, burners will need to be designed for oxidant and coal injection at specific points in the reaction space without seriously affecting product gas quality ($CO + H_2$ concentration) or process economics. TRW uses a staged combustion burner in its entrained-slagging combustor for $NO_x$ control, indicating that staged combustion may be compatible with the feeding methods for optimum syngas production.

The gasifier processes examined are designed to accomplish devolatilization and char burning in a single stage. Temperature and residence time are critical for ensuring near completion of these reactions in the gasification zone. A different set of temperature and residence time may be required to achieve optimum $NO_x$ or $SO_x$ precursor control. Residence times (or reaction space volume) for specific processes are not often reported and when they are, complete information is not provided to define

## TABLE 2-2. IN-PROCESS CONTROL REQUIREMENTS

| Control Variables | Dependence |
|---|---|
| Oxidant Staging | Burner Design |
| Residence Time in Gasifier/Slagging Zone | Reactor Volume<br>Coal, Steam, and Oxidant Flow Rates<br>Gasification Temperature<br>Coal Particle Size<br>Oxygen/Coal Ratio<br>Steam/Coal Ratio |
| Temperature | Oxygen/Coal Ratio<br>Steam/Coal Ratio<br>Oxidant<br>Heat Losses<br>Feed Stream Temperatures<br>Coal Composition |
| Temperature Zones<br>- Gasifier/Slagging<br>- Heat Recovery/Cooling | Reactor Design, Including<br>- Volume<br>- Heat Recovery<br>- Slag Removal |

TABLE 2-3. GASIFICATION PROCESSES

| Process | Texaco[4,5] | Shell[4,5] | KBW[4,5] | Saarberg-Otto[4,5] | TRW[10] | Koppers-Totzek[4,5] |
|---|---|---|---|---|---|---|
| Type Reactor | Vertical Cylindrical Downward Flow | T-Shaped Diametrically Opposed Burners | Square Column Upward Flow | Vertical Cylindrical | Off-Horizontal Cylindrical | Horizontal Ellipsoid Diametrically Opposed Burners |
| Pressure | 600 psig | 400 psig | Atmospheric | Elevated | Atmospheric | Atmospheric |
| Minimum Temperature[a] | 1250-1400°C | | | | | |
| Coal Feed | Slurry | Dry | Dry | Dry | Dry or Slurry | Dry |
| Oxidant | Oxygen | Oxygen | Oxygen | Oxygen | Air | Oxygen |
| Gas Cooling | Water quench or dry heat recovery | Combined with cool recycle gas followed by heat recovery | Heat recovery | Combined with cool recycle gas followed by heat recovery | None | Heat recovery followed by water quench |

[a] Typical slagging temperature for most coals.

the specific reaction zone and temperature. For slagging gasifiers, minimum temperature is determined by the fluid viscosity temperature of the slag which is in turn dependent on ash composition.[11] Exit temperatures reported of the gasification zone range from about 1200°C to 1650°C. Temperatures within the gasification zone, if reported, are viewed with caution because of dependence on location and on the way they were determined. As noted in Table 2-2, several operating variables and the heat loss affect this temperature. Table 2-4 shows the range among three processes that two of these variables, $O_2$/coal and steam/coal, exhibit. The data are for a single coal (Illinois No. 6). Table 2-4 also presents product quality ranges for product gases intended for combined cycle or heat generation uses. There is considerable disparity of $CO + H_2$ and $CO/H_2$ among the processes, largely affected by $CO_2$ levels. With respect to in-process controls, these data give some indication of the range of operating variables and of product quality within which operating conditions may be changed to optimize $NO_x/SO_x$ precursor control.

Particle size helps to determine the rate at which reactions approach completion or equilibrium and thus have an affect on residence time requirements. Coal may be fed dry or as a slurry, but slurry viscosity considerations determine which coal slurries are pumpable. Dry coal feed of 90 percent less than 100 μm are reported. Texaco reports 500 to 1,000 μm particle size in its coal slurry. It is anticipated that particle size will play an important role in schemes for in-process control.

Gasifier designs usually include two zones: the gasification zone and a cooling zone. Gasification zone geometry and burner placement are selected to allow gasification reactions to go to completion, thus providing maximum carbon conversion before the gas exits the gasification zone. The cooling zone provides a means for cooling the gas stream and one of three cooling methods is typically used:

- dry heat recovery, using radiant/convective coolers,
- direct water quench,

## TABLE 2-4. GASIFIER OPERATING VARIABLES AND PRODUCT QUALITY
## (ILLINOIS NO. 6 COAL)

| Variables | Texaco[7] | Shell[5] | KBW[4] |
|---|---|---|---|
| $CO + H_2$, mol % Dry | 77.0 | 97.1 | 88.6 |
| $CO/H_2$, mol ratio | 1.0 | 2.0 | 2.3 |
| $CO/CO_2$, mol ratio | 2 | 36 | 7 |
| $O_2$/Coal, w/w, MAF[a] | 1.04 | 0.94 | 1.00 |
| Steam/Coal, w/w, MAF | 0.6[b] | 0.1 | 0.1 |

[a] MAF: moisture, ash free.

[b] Includes slurry water.

- recycle of cool syngas, or in combination with dry heat recovery.

Some ash or solidified slag leaves the cooling zone with the gas, although the bulk of the molten slag is separated in the gasification zone. Cooling zone temperatures of 850°C to almost 1000°C are reported for dry heat recovery or syngas recycle. Texaco reports gas temperatures of 500-600°C at the exit of a water quench. Orientation and temperature of the cooling zone are of importance when considering injection of nitrogen and sulfur capture materials for in-process controls. One proposal includes injection into a low temperature region such as the cooling zone to avoid sintering effects. A significant drawback to this scheme is the increase in particle loading of the gas leaving the cooling zone.

In the preceding discussion, gasifier operation and design as they relate to possible in-process controls were examined. In-process controls of $NO_x/SO_x$ precursors included staged injection of the oxidant and of capture materials and manipulation of the operating variables. Some tentative conclusions can be drawn regarding the flexibility of gasification processes for the application of in-process controls from the following summary:

- Compatibility of oxidant feed for in-process controls with base case oxidant feed methods is undetermined. At least one entrained-slagging combustion process employs staged oxidant feed for $NO_x$ control.

- There is some latitude in manipulation of $O_2$/coal and steam/coal if needed for in-process control.

- There is considerable latitude in how much $CO + H_2$ and $CO/H_2$ can be varied and still produce an acceptable product.

- Compatibility of residence time for optimum in-process controls with base case residence times is undetermined.

- Two temperature zones within the gasifier provide a potential for staged injection of capture materials that will avoid or minimize sintering.

## 2.4 UNTREATED GAS COMPOSITION

Normally, only the composition of clean product gas after sulfur removal is reported. Sometimes, so-called raw gas compositions are reported but they are after removal of particulate matter and after scrubbing to remove ammonia. Table 2-5 presents a range of values for the minor constituents that are believed to represent gasifier effluent before any pretreatment reasonably well. Because several sources had to be accessed to complete the listing, Table 2-5 represents a composite taken from several compositions. Data sources are as follows:

$CH_4$: Shell design[8] using Illinois No. 6 coal and Texaco pilot plant data[5] using western bituminous coal

$N_2$: Texaco designs[3,6]

$H_2S$: Shell design[8] using Illinois No. 6 coal and KBW typical analysis[4] using Illinois No. 6 coal

COS: Same as $H_2S$

$CS_2$: Same as $H_2S$

$NH_3$: Shell design[8] using Illinois No. 6 coal. Higher value is estimated from $NH_3$ reported in the settler of Ruhrchemie Texaco gasifier using Illinois No. 6 coal[7]

HCN: Same as $H_2S$

### TABLE 2-5. RAW GAS MINOR CONSTITUENTS FOR OXYGEN-BLOWN GASIFIER OPERATION[d]

| | Mol %, Dry | N and S Oxidized State, lb/$10^6$ Btu[c] |
|---|---|---|
| $CH_4$ | 0.04 - 0.05 | - |
| $N_2$ | 0.4 - 0.8[a] | - |
| $H_2S$ | 1.11 - 1.90 | 6.25 - 10.70 |
| COS | 0.133 - 0.142 | 0.75 - 0.80 |
| $CS_2$ | 0.005 - 0.102 | 0.06 - 1.15 |
| $NH_3$ | 0.102 - 0.105 | 0.41 - 0.42 |
| HCN | 0.02 - 0.04 | 0.08 - 0.16 |
| NO | NR[b] | - |
| $SO_2$ | NR | - |

[a] Shell may be higher from $N_2$ padding of feed system.

[b] NR: not reported.

[c] Based on gas heating value of 300 Btu/scf. Thermal $NO_x$ formation neglected. $NO_x$ reported as $NO_2$; $SO_x$ formation reported as $SO_2$.

[d] This table represents a composite gas analysis taken from several sources as explained in the text.

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## 3.0 IN-PROCESS NITROGEN CONTROL - THEORY AND EXPERIENCE

The reactions which take place in an entrained bed gasifier can be grouped into the following general categories: coal devolatilization, combustion of volatiles, combustion and gasification of resulting char, homogeneous oxidation of carbon monoxide and hydrogen, and the steam reforming of methane.[1] Of these, only reactions in the first three categories play a significant role in the generation and fate of nitrogen and sulfur species in the gasifier.

### 3.1 COAL DEVOLATILIZATION

Upon being heated, coal begins to decompose at 350 to 400°C into a carbon-rich residue and a hydrogen-rich volatile fraction. This decomposition continues until a temperature typically around 950°C is reached which, if maintained for an extended period of time, results in a char with a structure approaching that of graphite. The volatiles emitted consist of various gases and liquids whose compositions and relative proportions depend on coal type and manner of heating.[2] The quantity of volatiles produced has been shown to be a function of several factors as summarized below:[3]

- Volatiles generally yield increases as particle size decreases.
- Changes in particle heating rate in the range of 600 to 50,000°C/sec produce very little effect on volatiles yield. Yield increases sometimes attributed to heating rate changes are probably due to conditions employed to achieve faster heating (i.e., well dispersed, smaller particles).
- Devolatilization at elevated pressure retards the escape of gaseous species and hence reduces volatiles yield.

- Coal type is an important variable. Anthony[2] found yields from Pittsburgh seam bituminous coal to increase with decreasing particle size and decreasing pressure, while yields from Montana lignite were independent of both pressure and particle size.

The products of devolatilization are chemically-produced water, gas, tar, and char. A number of modeling approaches for devolatilization have been proposed by various workers. One of the most comprehensive models was proposed recently by Reidelbach and Summerfield[4] and is illustrated in Figure 3-1. In this model coal becomes thermally activated and decomposed to either an intermediate char and primary gas or an intermediate char and tar. The intermediate char is each step further decomposes to produce secondary gas and final char. Primary tar also cracks to form final char and secondary gas. Two sets of data were successfully fitted to this model by adjusting 15 rate and stoichiometric parameters. (Such agreement is not surprising, however, given the large number of adjustable parameters).[5]

The gases formed during devolatilization contain primarily $CH_4$, $H_2$, CO, and $CO_2$ but will also contain lesser amounts of nitrogen and sulfur species. Axworthy found that significant amounts of HCN were evolved during pyrolysis. Blair found that nitrogen was evolved late in the devolatilization process as heavy organics which are likely further pyrolyzed to species like $NH_3$ and HCN.[6] Morley doped acetylene with known quantities of pyridine, $CCl_4$, and $CH_3CN$ and found that all fuel nitrogen was converted to HCN in the fuel-rich reaction zone; for fuel oil doped with pyridine, Gerhold found both HCN and $NH_3$ in significant quantities.[7]

Pershing and Wendt have studied the evolution of volatiles during fuel-rich coal combustion.[4] Their results for a Western Kentucky coal indicated that about 50 percent of the original coal mass was volatilized and that 40 to 50 percent of the original coal nitrogen was volatilized. The balance of the coal nitrogen remained with the char. Both total and nitrogen volatiles increased at higher oxygen stoichiometries probably due to higher pyrolysis temperatures resulting from increased combustion rates. It should be noted that total and nitrogen volatile yields will likely be

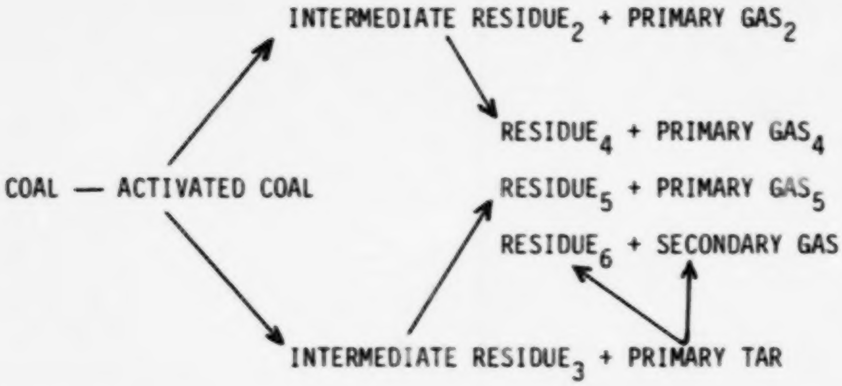
INTERMEDIATE RESIDUE$_2$ + PRIMARY GAS$_2$
RESIDUE$_4$ + PRIMARY GAS$_4$
COAL — ACTIVATED COAL
RESIDUE$_5$ + PRIMARY GAS$_5$
RESIDUE$_6$ + SECONDARY GAS
INTERMEDIATE RESIDUE$_3$ + PRIMARY TAR

Figure 3-1. Coal pyrolysis model of Reidelbach and Summerfield.

Source: Reference 4.

lower under pressurized gasifier conditions (i.e., higher pressure and lower temperature) than the results cited above for combustion conditions. For atmospheric gasification, only the temperature effects will be a factor. A volatile nitrogen yield of 40 to 50 percent is probably a maximum to be expected in a pressurized entrained-bed gasifier.

The rate of coal devolatilization under combustion conditions is quite fast. Data showed that devolatilization of particles 53 μm in diameter at 1097°C was at least 98 percent complete in 75 msec. Another study indicated that devolatilization was complete in 80 msec for particles with a size distribution typical of pulverized coal.[8] Char burnout, by comparison, generally required more than 300 msec.[9]

## 3.2 COMBUSTION OF VOLATILES

Several studies in the literature indicate that volatile nitrogen species are oxidized to NO in the gasifier and subsequently undergo homogeneous and heterogeneous reactions. According to theory, oxygen approaching the char surface meets and preferentially reacts with volatilized species.[10] Measurements of nitrogen species in an experimental entrained-bed gasifier by Price showed significant quantities of NO being formed.[11] The concentration of oxidized species increased to a maximum as axial distance from the injection point increased and then began to decline. Effluent concentrations of NO were significant but complete char burnout was not achieved in the gasifier. In other studies, and the data reported in Section 2.0, NO levels in the gasifier effluent are negligible. These results suggest that HCN and other fixed nitrogen species are oxidized quickly to NO shortly after devolatilization. As the gas becomes more fuel-rich (due to gasification of char by $CO_2$ and $H_2O$) NO is reduced to $N_2$.

A mechanism which may explain this behavior has been proposed by Peterson.[12] In this model, fuels with a multiple-bonded CN structure such as coal decompose from five- and six-membered heterocyclic rings to single rings (the pyridine structure) and produce HCN as the main nitrogeneous product of pyrolysis. Table 3-1 summarizes the nitrogen reactions in the

Peterson model. The HCN liberated by pyrolysis is destroyed via three reaction paths: direct formation of HNCO, direct formation of NCO, and formation of NCO from CN. Further reactions occur to form $NH_2$ and NH by reaction with H atoms. The final steps of the mechanism all involve amine radicals ($NH_2$, NH, and N). Ammonia ($NH_3$) formation occurs by simple H atom transfer processes. NO formation occurs by the reaction of an amine radical with O, OH, and $O_2$. Amine radicals can further react with NO to produce $N_2$ and $N_2O$. In the flames investigated, $N_2O$ and HNO form $N_2$ and NO, respectively. All reactions in Table 3-1 were considered to be irreversible except for those converting to $NH_3$ to $NH_2$ and CN to HCN.

The validity of the mechanism described above has been tested against experimental combustion data. Peterson, et al., used the model to predict nitrogen species profiles for lean, stoichiometric, and rich flames; good agreement was achieved between experimental and predicted profiles.[13] Glass showed that a simplified version of the Peterson mechanism could be used to predict the fate of nitrogen species from Utah bituminous coal in fuel-rich flames.[14] Wendt expanded this work and showed the mechanism applied to a wider range of coals and temperatures.[15]

Miller, et al., developed a mechanism similar to the Peterson model and found good agreement between experimental results and flame structure calculations based on the mechanism.[22] Miller found that the most important and rate controlling step for HCN destruction was the reaction with oxygen atoms unlike Peterson and others who generally favored reactions with OH to produce HNCO and HOCN. Miller's reactions for the formation of NO and conversion of NO to $N_2$ agree with those of Peterson, Glass, and Wendt.

## 3.3 CHAR GASIFICATION AND COMBUSTION

The nitrogen which is not devolatilized during pyrolysis is consumed during combustion and gasification of the resulting char. If sufficient oxygen is available, char nitrogen will oxidize to form NO. More likely, oxygen will be depleted by combustion of volatiles and carbon and char nitrogen will evolve as HCN. In either case, the gaseous nitrogen species

## TABLE 3-1. FUEL-NITROGEN REACTIONS IN THE PETERSON MODEL

| | |
|---|---|
| Coal Pyrolysis | |
| $\text{Coal-N} + 2O_2 \rightarrow HCN + CO + H_2$ | assumed irreversible and infinitely fast |
| HCN Destruction | |
| $HCN + O \rightleftharpoons NCO + H$ | 1 |
| $HCN + OH \rightleftharpoons HNCO + H$ | 2 |
| $CN + H_2 \rightleftharpoons HCN + H$ | 3 |
| $CN + O_2 \rightleftharpoons NCO + O$ | 4 |
| $NCO + H \rightleftharpoons NH + CO$ | 5 |
| $NCO + H_2 \rightleftharpoons HNCO + H$ | 6 |
| $HNCO + H \rightleftharpoons NH_2 + CO$ | 7 |
| Amine Interconversion | |
| $NH_2 + H \rightleftharpoons NH + H_2$ | 8 |
| $NH_2 + OH \rightleftharpoons NH + H_2O$ | 9 |
| $NH + H \rightleftharpoons N + H_2$ | 10 |
| $NH + OH \rightleftharpoons N + H_2O$ | 11 |
| $NH + O \rightleftharpoons N + OH$ | 12 |
| $NO$, $N_2$ and $N_2O$ Formation | |
| $NH_2 + NO \rightleftharpoons N_2 + H_2O$ | 13 |
| $NH + NO \rightleftharpoons N_2O + H$ | 14 |
| $N + NO \rightleftharpoons N_2 + O$ | 15 |
| $NH_2 + O \rightleftharpoons HNO + H$ | 16 |
| $NH + O \rightleftharpoons NO + H$ | 17 |
| $N + OH \rightleftharpoons NO + H$ | 18 |
| $N + O_2 \rightleftharpoons NO + O$ | 19 |
| $N_2O + H \rightleftharpoons N_2 + OH$ | 20 |

(Continued)

TABLE 3-1. FUEL-NITROGEN REACTIONS IN THE PETERSON MODEL (CONTINUED)

| | |
|---|---|
| $NH_3$ Formation | |
| $NH_3 + O \rightleftharpoons NH_2 + OH$ | 21 |
| $NH_3 + OH \rightleftharpoons NH_2 + H_2O$ | 22 |
| $NH_3 + H \rightleftharpoons NH_2 + H_2$ | 23 |
| $NH_2 + NO_2 \rightleftharpoons NH_3 + O_2$ | 24 |
| $NH_2 + H + M \rightleftharpoons NH_3 + M$ | 25 |

Note: M is any particle or reaction surface.

Source: Reference 12.

will combine with other gaseous species and react according to a mechanism similar to Table 3-1.

## 3.4 CONDITIONS WHICH PROMOTE IN-PROCESS NITROGEN CONTROL

Since both HCN and $NH_3$ in gasifier exit gas will be converted to $NO_x$ by subsequent combustion of that gas, the objective of in-process control in the gasifier will be to convert a maximum fraction of fuel nitrogen to $N_2$. A number of studies have been conducted involving fuel-rich combustion of coal in which these same phenomena have been examined. The results of these studies can be applied to entrained-bed gasifiers to suggest trends which might result from changes in process and operating variables. In their study of fuel nitrogen conversion in lean to rich flames, Peterson, et al., found that maximum conversion to $N_2$ occurs at a stoichiometric ratio (SR) of about 0.75 operating on Illinois No. 6 coal at an $O_2$/coal ratio of 0.86.[16] This compares to a SR of about 0.4 for a Texaco entrained-bed gasifier. An increase of the SR could be achieved by raising the oxygen to coal feed ratio. Increasing the $O_2$/coal ratio will also have the effect of increasing gasifier temperatures.

In their study of fuel-rich flames, Wendt, et al., found that fuel nitrogen conversion to $N_2$ is approximately 60 to 70 percent at SR equal to 0.6 and about 75 to 85 percent at SR equal to 0.8 for long residence times (1.5 to 2.5 seconds).[17] This result is consistent with that reported by Peterson above. At lower SRs, cooling of the reactor (by 50 to 100°C) generally decreased the conversion to $N_2$; at higher SRs, cooling had no significant effect. Experimental results showed that small coal particles (less than 53 μm) produce less NO under fuel-rich conditions and that the overall conversion of fuel N to $N_2$ is greater. The rate of devolatilization (faster for smaller particles), which affects the post-flame levels of nitrogeneous species, is thought to be the controlling mechanism. Following this same line of reasoning, other factors which increase the rate of devolatilization, such as lower pressure, may also act to increase the conversion of fuel nitrogen to $N_2$. In support of this theory, the

Koppers-Totzek process, which operates at atmospheric pressure, is characterized by lower $NH_3$ levels than the pressurized entrained-bed gasifiers.

Song and Bartok also investigated the reduction of HCN, $NH_3$, and NO to $N_2$ during fuel-rich combustion of methane in air. Their early work showed that conversion to $N_2$ can be accelerated toward equilibrium by increasing the temperature.[18] Analysis of experimental data suggested that the rate of $N_2$ formation should be accelerated by replenishment of the pool of free radical chain carriers (O + H + OH) in the reaction time range of 50 to 75 ms at 1,580-1,680°C. Song and Bartok showed in a subsequent study that the conversion efficiency to $N_2$ was improved by 15 to 25 percent (relative to the baseline) when 0.5 percent $O_2$ (based on total gas flow) was injected about 50 to 100 ms downstream from the flame zone. With $O_2$ injection, over 80 percent of the original nitrogen species were converted to $N_2$. The $O_2$ injection did not alter bulk concentrations or temperature and flow profiles. These results suggest a possible relaxation of the high temperature requirement for the reduction of fixed nitrogen species to $N_2$ in fuel-rich combustion or partial oxidation (i.e., gasification).[19]

In summary, the following process parameter changes are suggested as a means to increase the conversion of fuel nitrogen to $N_2$ in an entrained-bed gasifier:

- operate at higher $O_2$/coal-fired ratios and hence higher temperatures,
- decrease the particle size of feed coal,
- decrease gasifier operating pressure, and
- inject a small amount of $O_2$ 50 to 100 ms downstream of flame zone in the gasifier.

With the exception of the impact of pressure on devolatilization (whose effect is coal-specific), the results discussed above at atmospheric pressure are expected to be similar to those at elevated pressures. A review of the Table 3-1 reactions shows that most of the gas-phase reactions included in the Peterson model have equal moles in both the reactants and products. Thus pressure changes will not substantially affect these reactions.

Under typical pressurized entrained-bed slagging gasifier conditions (oxygen-blown mode), 85 to 90 percent of the fuel nitrogen which enters the gasifier is converted to $N_2$.[20] Most of the remaining coal nitrogen exits the gasifier as $NH_3$ and HCN in the raw gas (a small amount of nitrogen is retained in the slag). Based on the high-end concentrations for $NH_3$ and HCN presented in Table 2-5, the combustion of this fuel gas in a new gas turbine or boiler will generate fuel $NO_x$ (as $NO_2$) emissions at a rate of 0.58 lb/million Btu. Table 2-1 indicates that the $NO_x$ emission limits for new facilities are about 0.278 lb/million Btu for gas turbines and 0.5 to 0.7 lb/million Btu for boilers. This implies that approximately 50 percent of the exit gas-fired nitrogen species (e.g., $NH_3$ and HCN) must be converted to $N_2$ in the gasifier if this fuel gas is to be combusted in a gas turbine without additional $NO_x$ control techniques. Thus the fuel nitrogen conversion to $N_2$ in the gasifier must be raised from normal levels of 85 to 90 percent to 95 percent or greater. For boiler combustion of the gasifier fuel gas, no additional fixed nitrogen species reduction or $NO_x$ control techniques would be required to meet NSPS limitation. In most cases, additional $NO_x$ control will not be required for retrofit boiler applications as well since $NO_x$ emission limitations for existing boilers are generally less stringent than NSPS.

The objective of the process changes described in this section would be to raise the fraction of fuel nitrogen that is converted to $N_2$ from typical levels of 85 to 90 percent to 95 percent or greater for gas turbine applications. It is not possible, at this time, to project the $N_2$ conversion that would result from the recommended changes due to the complex interactions of process parameters and their effect on gas composition. A validated process model and/or experimental data collected under representative conditions would be most useful in this regard.

Finally, it should be noted that a small amount of $NH_3$ in the fuel gas directed to a gas turbine combustor or boiler may have a beneficial effect on $NO_x$ formation in these devices. One new process for controlling $NO_x$ emissions from stationary combustors is Exxon's Thermal $DeNO_x$ Process, whereby NO is reduced by $NH_3$ in the presence of $O_2$.[21] This process will be examined in Task 2 of this study to determine its applicability to the gasifier-combustor system and to identify the quantity, if any, of $NH_3$ that would be desirable in the gasifier exit gas.

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## 4.0 IN-PROCESS $SO_x$ CONTROL THEORY AND EXPERIENCE

In order to develop the in-process controls for $SO_x$ and $NO_x$ precursors generated in the gasifier, it is necessary to attempt to understand all the possible reactions of nitrogen and sulfur taking place under a given set of typical conditions. The reducing atmosphere in the gasifier is assumed to approximate the fuel-rich zone (i.e., first stage) conditions of the LIMB process.[1] The information collected on the release of sulfur from coal in the fuel-rich zone of the LIMB process may be applied here to allocate the sulfur between the slag (solid) phase and gas phase. Additional insight into the chemistry of coal sulfur reactions in a reducing atmosphere is offered by Attar[2] and Freund, et al.[3]

Sulfur may be present in coal in any of the following three forms:

- organic sulfur,
- elemental sulfur, and
- inorganic sulfur.

The organic sulfur includes all the sulfur bound to the hydrocarbon matrix. The exact groups which are present in the coal are unknown. The most important divalent sulfur compounds in fossil fuels are known to be thiophenes, aryl sulfides, cyclic sulfides, aliphatic sulfides, and aryl aliphatic thiols.

The inorganic sulfur is present as disulfides and sulphates. The total sulfur in coal typically varies between 1 and 3 weight percent. The amount of organic sulfur plus elemental sulfur is usually one-half to one-third of total sulfur. Most inorganic sulfur is in the form of $FeS_2$. The amount of sulphate sulfur rarely exceeds 0.1 weight percent and is usually negligible.

During coal combustion, sulfur release seems to occur in a discontinuous manner. The two principal periods of sulfur release are: (a) during devolatilization under reducing conditions and (b) during char burning under oxidizing conditions. The first and dominant period of sulfur release occurs during devolatilization and involves organic sulfur and partial decomposition of pyrites (inorganics). The second period of sulfur release seems to be caused principally by the decomposition of metal sulfides in an oxidizing atmosphere (Figure 4-1).

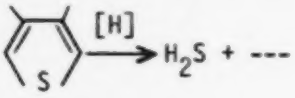
In the review article, Attar[2] examined the kinetics and thermodynamics of the following three types of reactions of organic sulfur groups: (1) thermal degradation, (2) hydrogenation, and (3) interactions of $H_2S$ and S (elemental or polymeric sulfur). It was observed that hydrodesulfurization is a thermodynamically favored reaction but complete hydrodesulfurization of organic sulfur does not occur below 1400°C.

In fact, the study of sulfur release in the manufacture of coke suggests that the sulfur evolution rate from char reaches a minimum around 700 to 800°C. Evolution again commences around 1100°C. These observations were attributed to mass transfer limitations in the range of 700 to 800°C. The reduction in the surface area limits the accessibility of $H_2$ to the sulfur. Trapping of sulfur in the form of stable heterocyclic organic compounds is also believed to account for its presence in high temperature char. Price[6] found substantial amounts of sulfur retained in the char before complete burnoff in a test entrained bed gasifier. Such reactions are thermodynamically favorable, and the sulfur which does react to form heterocycles remains trapped because these thiophenes (heterocycles) are kinetically stable. Applying this information to the entrained-bed gasifier indicates that some organic sulfur will find its way into the slag as trapped thiophenes. When the temperature exceeds 1100°C, more $H_2S$ will be released. At and above 1400°C, the hydrodesulfurization may be complete and all organic sulfur may be devolatilized in the gasifier.

Organic sulfur species such as thiophenes, and other sulfur products such as COS and $CS_2$ may all be represented by $H_2S$ chemistry to depict the role of organic sulfur in coal combustion under gasifier conditions. In other words, the reactions shown below may be represented by $H_2S$ in the gasifier.

$$\text{R-S-H} \xrightarrow{[H]} H_2S + \text{---} \qquad (4\text{-}1)$$

$$\text{R-S-R}' \xrightarrow{[H]} H_2S + \text{---} \qquad (4\text{-}2)$$



(4-3)

$$nS \longrightarrow Sn \longrightarrow H_2S \qquad (4\text{-}4)$$

$$C + S_2 \longrightarrow CS_2 \qquad (4\text{-}5)$$

$$COS + H_2S \rightleftharpoons CS_2 + H_2O \qquad (4\text{-}6)$$

$$CO_2 + H_2S \rightleftharpoons COS + H_2O \qquad (4\text{-}7)$$

At gasifier temperatures of 1500 K and above, all the reactions shown in Table 4-1 may be included in the devolatilization step and may be represented by the hydrodesulfurization reaction: $S + H_2 \rightleftharpoons H_2S$. Attar reviewed the reactions of sulfur in the coal-gas reaction and summarized his findings as follows:

- The kinetics and thermodynamics of $H_2S$ reactions hold the key to the ultimate distribution of sulfur in coal pyrolysis. The overall scheme of interaction can be visualized using Figure 4-2.

- Most of the inorganic sulfur that is volatilized is released below about 800°C because (a) $FeS_2$ is reduced almost completely to FeS and $H_2S$ below 800°C. FeS is rather stable and releases very little of its sulfur; (b) the rate of reaction of $H_2S$ with the basic minerals is so large above about 700°C that, even when the

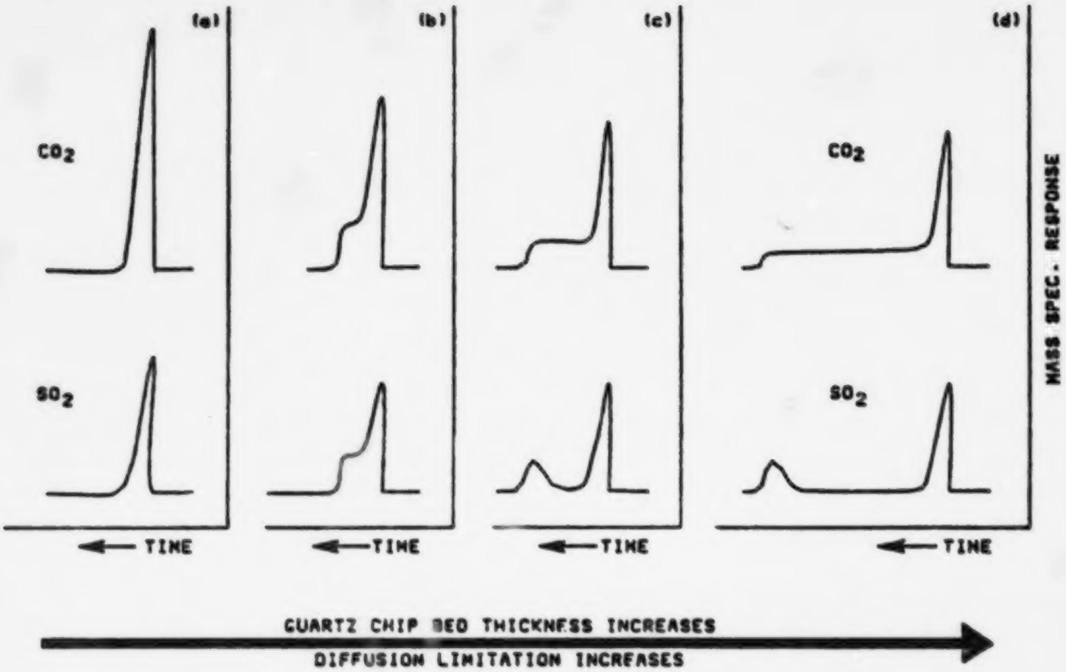
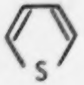
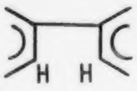
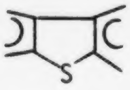


Figure 4-1. Discontinuous sulfur release in the coal combustion reaction under non-steady state conditions.[4]

TABLE 4-1. THERMODYNAMICS OF THE TRANSFORMATION OF SULFUR FUNCTIONAL GROUPS IN COAL AT 600 K[4]

| | | $\Delta H^\circ_{600}$ (kJ/mol) | $\Delta S^\circ_{600}$ (kJ/mol) | $\Delta F^\circ_{600}$ (J/mol K) |
|---|---|---|---|---|
| A | $R\text{-}SH + H_2 \longrightarrow RH + H_2S$ | -62.5 | 13.4 | -54.5 |
| B | $\phi\text{-}SH + H_2 + H_2 \longrightarrow \phi H + H_2S$ | -54.1 | 15.5 | -63.4 |
| C | $(C_2H_5)_2S + 2H_2 \longrightarrow 2C_2H_6 + H_2S$ | -116.0 | 36.5 | -138.0 |
| D | $\text{Cyclo-}C_4H_8S + 2H_2 \longrightarrow C_4H_{10} + H_2S$ | -68.0 | 9.5 | -73.7 |
| E | $\phi_2S + 2H_2 \longrightarrow 2\phi H + H_2S$ | 14.9 | -64.3 | 61.2 |
| F |  $+ 2H_2 \longrightarrow C_6H_6 + H_2S$ | -35.9 | -173.2 | 68.0 |
| G | $(CH_3S)_2 + 3H_2 \longrightarrow 2CH_4 + 2H_2S$ | -177.1 | 5.0 | -174.1 |
| H | $RHC{=}CHR + H_2S \longrightarrow RCH_2CH(SH)R$ | -91.4 | -298.0 | 87.5 |
| I | $RHC{=}CHR + RCH_2CH(SH)R \longrightarrow R(CH_2)_2CH(SHR\ CH_2R)CH_2R$ | -127.7 | -222.0 | 5.6 |
| J | $CH_3CH_2OH + H_2S \longrightarrow CH_3CH_2SH + H_2O$ | -30.0 | 1.0 | 30.6 |
| K | $\phi OH + H_2S \longrightarrow \phi SH + H_2O$ | -12.6 | -34.5 | 8.1 |
| L |  $+ H_2S \longrightarrow$  $+ 2H_2$ | 121.2 | 216.4 | -8.7 |

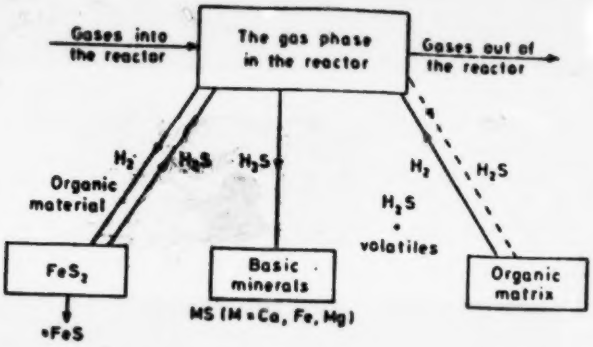

Gases into the reactor
The gas phase in the reactor
Gases out of the reactor
H₂
H₂S
Organic material
H₂S
H₂
H₂S
H₂S + volatiles
FeS₂
+FeS
Basic minerals
MS (M = Ca, Fe, Mg)
Organic matrix

Figure 4-2. Schematics of the dominant modes of reactions of sulfur in coal in reducing environment.[2]

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contact time is small, most of the $H_2S$ sulfur is trapped as metal sulfides (MS), (c) the porous structure of the organic material collapses around 800 to 860°C and thus further hydrodesulfurization becomes impossible, because of mass transfer limitations. Particles of FeS and MS may be trapped by the char and thus they are rendered inert or inaccessible to hydrodesulfurization.

- The sulfur that is volatilized above 800°C is released at a rate which is proportional to the rate of volatilization of the organic material. Most of this sulfur is in the form of $H_2S$ and $CS_2$.
- Only a small fraction of the sulfur is released in the form of organosulfur compounds (other than $CS_2$). At high temperatures, $H_2S$ and $CS_2$ are the only stable species that can survive the secondary reactions in the gas phase. The organic sulfur compounds that can be formed in the decomposition reactions at low temperatures are mainly thiophenes and low-molecular-weight sulfides, mercaptans, and disulfides. The thiophenes are products of the decomposition of the organic matrix or products of secondary reactions of organic materials with $FeS_2$. The aliphatic sulfides, mercaptans, and disulfides are products of secondary reactions in the gas phase.
- Hydrodesulfurization of coal above about 1,200 to 1,300°C results in almost complete gasification of the solid and, naturally, almost complete conversion of the sulfur to $H_2S$. This occurs because the disassociation of molecular hydrogen to atoms becomes appreciable. The rate of attack of H on the organic C-S and C-C bonds is large and effects an increase in the rate of gasification.

The inorganic sulfur, represented as iron pyrite ($FeS_2$), is disassociated into iron sulfide and elemental sulfur.

$$FeS_2 \xrightarrow{800°C} FeS + 1/2\ S_2 \qquad (4\text{-}8)$$

Hydrogen released in the gasifier at this temperature will also reduce the pyrites into iron sulfide.

$$FeS_2 + H_2 \xrightarrow{800°C} FeS + H_2S \qquad (4\text{-}9)$$

The sulfur released in all the above reactions is in the devolatilization step. The $H_2S$ formed in these reactions may in turn react with the mineral components of ash, e.g.,

$$CaCO_3 + H_2S \longrightarrow CaS + H_2 + CO_2 \qquad (4\text{-}10)$$

$$CaO + H_2S \longrightarrow CaS + H_2O \qquad (4\text{-}11)$$

The metal sulfides such as FeS or CaS formed in the ash probably react with oxygen before completion of burnout of ash particles.

$$FeS_x \xrightarrow{O_2} x\ SO_2 + \text{iron oxides} \qquad (4\text{-}12)$$

From the reactions cited above, one would expect the formation of $H_2S$ under reducing conditions. However, in an independent set of experiments for studying $CaO\text{-}FeS_2$ reactions and the formation of CaS, Levy, et al.[1] studied the decomposition of pyrites by lime under a nitrogen atmosphere. It was found that two major reaction products from the reaction mixture were elemental sulfur and sulfur dioxide.

$$4\ CaO + 3\ FeS_2 \rightarrow 4\ CaS + Fe_3O_4 + S_2 \qquad (4\text{-}13)$$

$$S_2 + CaO \rightarrow CaS + SO \qquad (4\text{-}14)$$

$$2\ SO \rightarrow SO_2 + \frac{1}{2} S_2 \qquad (4\text{-}15)$$

The experiments were conducted with varying ratios of Ca to S. The percent sulfur retained in the solid was calculated assuming that the total sample weight loss was solely due to the volatile products observed from the reaction, i.e., due to the release of elemental sulfur and the $SO_x$ formed. The assumption was justified since negligible oxygen was found in the $S_2$ and $SO_x$ mixture. It was found that about 2-1/2 percent of the sulfur in pyrites could be converted to $SO_2$ in an atmosphere of nitrogen independent of temperature in the range of 575to 1,100°C and independent of the CaO/coal ratio. This may be due to an impurity in the pyrites.[1] Any proportion of metal oxides, such as calcium oxide in ash, probably will result in the generation of $SO_2$ by this mechanism.

In summarizing the chemistry and mechanism of sulfur release during coal combustion, A. J. Moffat[4] concludes that the sulfur retention by ash seems to be favored by:

- lower particle temperature,
- available base minerals,
- reducing gaseous environment, and
- incomplete char burnout.

Since most of the sulfur is released during devolatilization, the most opportune time for scavenging this sulfur is probably right after devolatilization and just before volatiles combustion. One of the ways of effecting this control in gasifiers is to add alkaline oxides, for example lime, to the gasification reactors.

The use of lime in entrained-bed gasification is indicated in work reported by TRW.[7,8] In principle, $NO_x$ pollutants are converted to molecular nitrogen by manipulating the burner design and operating conditions, whereas sulfur compounds are removed in the slag by reaction with an additive such as lime. An $SO_2$ reduction of 40-60 percent is claimed[7] at a high slag removal rate of 80-90 percent.

From the available desulfurization information in other types of gasifier/combustor systems, it is apparent that the addition of alkaline oxides such as lime may offer the only practical solution to in-process control of sulfur species in entrained-bed slagging gasifiers. Other sources of alkaline metal oxides may be considered as additives to the gasifier. The effects of additives on both $NO_x$ and $SO_x$ precursors are discussed in the next section.

The information presented in Table 2-4 indicates that the combustion of fuel gas from a typical entrained-bed slagging gasifier in a gas turbine or boiler might generate up to 12.65 lb $SO_2$/million Btu (based on high-end gas concentrations) if no additional sulfur control techniques are applied. The sulfur content of fuel gas for a gas turbine is limited to low levels (typically around 20 ppm) due to materials considerations. Greater than 90 percent sulfur reduction would be required for new boiler applications to meet NSPS levels as summarized in Table 2-1. For retrofit boiler applications, this requirement will likely be lower and may depend on state and local regulations. The discussion presented above implies that it would be difficult to accomplish all of this required sulfur reduction using in-process sulfur controls in the gasifier alone. However, the extent to which sulfur can be captured in the gasifier will reduce the size and expense of downstream sulfur reduction equipment.

## 4.1 REFERENCES

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# 5.0 GASIFIER IN-PROCESS CONTROLS FOR NITROGEN AND SULFUR SPECIES

The literature search for nitrogen and sulfur species controls in the entrained-bed slagging gasifier revealed that, in general, nitrogen species control can be attained by manipulating the operating conditions to produce molecular nitrogen ($N_2$), and the sulfur species control can be achieved by the downstream treatment of product gas. The use of alkaline oxides, mainly lime (CaO), has been investigated for coal desulfurization technologies and gasification technologies other than entrained-bed slagging systems. No work discussing the effect of lime addition to the entrained-bed slagging gasifier has been reported. However, information from other processes such as lime injection multiple-burner (LIMB) technology[1], staged combustor technology[2], and others may be extrapolated to an entrained-bed gasifier.

Interestingly enough, the literature appears to address either the issue of $SO_x$ control or $NO_x$ control. Very few attempts to consider the effect of alkaline oxides on gasifier intermediates such as HCN or $NH_3$, which are precursors for $NO_x$, have been noted. An attempt is made to consider in this discussion the $NO_x$- and $SO_x$-related reactions together.

It has been noted that higher ash content in the feed coal promotes sulfur capture in the slag by contributing added alkaline material. The ash in feed coal is composed mainly of alkaline metal oxides such as calcium oxide, magnesium oxide, potassium oxide, etc. It is clear, then, that basic metal oxides react chemically with sulfur compounds and act as scavengers. The prime candidate for use as a sorbent for desulfurization is lime or calcium oxide. The effect of lime addition to an entrained-bed gasifier is discussed in this section. Sulfur and nitrogen reactions with other absorbents besides lime are also considered.

The theories and mechanisms for the release of sulfur and nitrogen compounds from feed coal have been previously discussed. The reactions taking place in the gasifier are comparable to the reactions taking place in the reducing atmosphere of the first-stage combustor in TRW-type stage combustors[2] or the first stage of a LIMB technology combustor.[1]

One study[3], also reported in Section 4.0, reported measurement of sulfur and nitrogen species along the axis of a test gasifier. Included, along with $N_2$, were HCN, $NH_3$, NO, $H_2S$ and $SO_2$. It is of interest to evaluate and estimate the effect of CaO on the generation or destruction of these pollutants under gasifier conditions.

## 5.1 EFFECT OF CALCIUM OXIDE ON FUEL-NITROGEN DERIVED POLLUTANTS

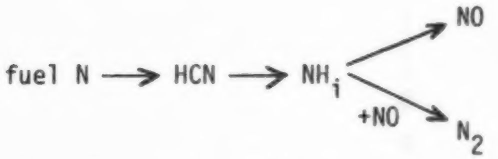
As has been previously discussed, the fuel nitrogen reactions are involved in all three major steps of coal combustion:

- fuel devolatilization leading to HCN,
- combustion of volatiles, and
- char gasification.

These reactions are considered in earlier sections. The effect of the addition of CaO on these reactions at gasifier temperatures and pressures in highly reducing atmospheres are discussed here.

### 5.1.1 Fuel Devolatilization

As discussed in Section 3.2, most workers in the field generally believe that the mechanism for converting fuel nitrogen to NO and $N_2$ can be considered as follows:[4,5]



$$\begin{tikzcd} & & & NO \\ \text{fuel N} \arrow[r] & HCN \arrow[r] & NH_i \arrow[ur] \arrow[dr, "+NO"'] & \\ & & & N_2 \end{tikzcd} \qquad (5\text{-}1)$$

This mechanism shows that HCN is the main nitrogenous product of devolatilization and is the primary intermediate in the formation of $NH_i$ (including $NH_3$), NO, and $N_2$. The addition of CaO to an entrained-bed slagging gasifier is not expected to alter the rate of fuel nitrogen compounds or the infinitely fast rate of formation of HCN. The addition of lime to the coal feed stream may affect the heat transfer to the coal particles to a minor extent but should not affect the generation rate of hydrogen cyanide. The addition of lime does, however, affect the reactions involving hydrogen cyanide and its products of combustion/decomposition as described below.

### 5.1.2 Combustion of Volatiles

As discussed in Section 3.0, HCN reacts with O, OH, and H immediately after formation to produce NCO, HNCO, and CN. These species, in turn, participate in other reactions as outlined in Table 3-1. If CaO is added to the gasifier, competing reactions between CaO and HCN would significantly affect the concentration of HCN. If a portion of the HCN normally formed is effectively removed from the gasifier reaction mix by complexing with CaO, the amount of $NH_3$, NO, NCO, HNCO, CN and $N_2$ subsequently formed will also be reduced. The concentration of these final nitrogen products exiting the gasifier would be reduced in roughly the same proportion as the amount of HCN complexed by CaO. For example, if the exit gas from a gasifier contained 6000 ppm $N_2$, 2000 ppm $NH_3$, and 300 ppm HCN under normal operating conditions, and CaO was added to the gasifier and reacted with one-half of the HCN produced during devolatilization, the new exit gas would be expected to contain approximately 3000 ppm $N_2$, 1000 ppm $NH_3$, and 150 ppm HCN.

In the gasification and combustion literature examined during this study, no mention was made of the possible reactions between CaO and HCN. However, acidic HCN and basic CaO are expected to undergo a neutralization reaction. It may also be important to consider the reactions of HCN and CaO in the presence of CO, $CO_2$, NO, $SO_2$, $H_2S$, $H_2$, OH, N, etc. Literature review of these reactions between CaO and HCN did not yield satisfactory results. A Chemical Abstracts Data Base search provided some information on the reaction chemistry of HCN and CaO. The high temperature product of the reaction of HCN and CaO is calcium cyanamide, $CaCN_2$. The possible reactions and intermediates are:

$$\mathrm{HCN + CaO}\begin{array}{l}\nearrow \mathrm{Ca(CN)_2 + H_2} \qquad\quad 200\ \text{to}\ 700^\circ\mathrm{C}\\ \rightarrow \mathrm{Ca(NCO)_2 + CaCN_2} \quad 200\ \text{to}\ 700^\circ\mathrm{C}\\ \searrow \mathrm{CaCN_2\ or\ CaNCN} \qquad 700\ \text{to}\ 1{,}100^\circ\mathrm{C}\end{array} \qquad (5\text{-}2)$$

According to the abstract from the publication of Polyanchikov, et al.,[6] the course of the reaction between gaseous HCN and CaO at 300 to 600°C fits well with the formal overall reaction kinetics. The rate is diffusion-controlled in the temperature interval 600 to 1,100°C. Intensive sintering of the reaction mass occurs at 200 to 400°C likely due to the formation of $Ca(NCO)_2$ and $Ca(OH)_2$. The content of $CaCN_2$ in the reaction product increases to 93.5 ± 2.86 percent at 800°C and the amount of products such as $Ca(CN)_2$, $Ca(NCO)_2$, and $CaCO_3$ decreases with increasing reaction temperatures. The products formed will depend, of course, on the temperature of the zone in which CaO is injected. Further discussion of temperature effects on CaO reactivity is presented in Section 5.2. The process mechanism for Reaction 5-2 is proposed as a series of elementary mono- and bi-molecular reaction steps involving $Ca(CN)_2$ and $Ca(NCO)_2$ as intermediate products. $CaCN_2$ is characterized as a stable solid subliming at 1,300°C and may be incorporated into the slag. No information on the kinetics or thermodynamic stability of these compounds in a reducing atmosphere was found.

One would expect that the rate of reaction between HCN and CaO will parallel the rate of reaction between $H_2S$ and CaO since both HCN and $H_2S$ are acidic gases. During the absorption of $H_2S$ by lime, the rate of reaction is found to be dependent on the reaction temperature and the desurfacing of CaO. Calcination or surface activity is dependent on temperature and plays an important role in the absorption of the acid gas as will be discussed later. Probably such a phenomenon is important in the CaO + HCN reaction also.

In addition to reactions with HCN, CaO also has the potential to interact with other nitrogen intermediaries as presented in Table 3-1. Lime is not expected to be a factor in the reactions involving amine interconversions or ammonia formation due to the basic nature of these species. The addition of CaO to the gasifier may affect the formation of NO, $N_2O$, and $N_2$ if $NO_x$ species are absorbed by CaO. That such reactions exist at low temperatures is indicated by the development of dry FGD scrubbers which remove $NO_x$ by using a lime slurry containing some sodium hydroxide. The details and chemical reactions involved are not known. Similarly, the hydrated nitrogen oxides are acidic in nature and may be scavenged by CaO. These reactions have not been studied under gasifier temperatures and pressures.

### 5.1.3 Char Gasification and Combustion

The discussion in Section 3.3 indicates that the nitrogen remaining in the char will be converted either to HCN or NO which, in turn, will participate in the gas-phase reactions indicated in Table 3-1. As discussed above, CaO has the potential to react with both HCN and NO and thereby reduce the overall concentration of gas-phase nitrogen species. In addition to these reactions, the addition of lime to the gasifier will probably create conditions similar to those encountered in the manufacture of calcium carbide:

$$CaO + C \longrightarrow CaC_2 + CO \qquad (5\text{-}3)$$

Calcium carbide under these conditions and in the presence of steam may regenerate calcium oxide.

$$CaC_2 + H_2O \longrightarrow C_2H_2 + CaO \qquad (5\text{-}4)$$

Acetylene as a product in the reactor gases will boost their Btu value.

In summary, the addition of CaO to an entrained-bed slagging gasifier is expected to have a beneficial effect by reducing the overall concentration of nitrogen species in the exit gases. This effect will be achieved by the reaction of CaO with HCN, which is the primary nitrogen species intermediary product of fuel nitrogen pyrolysis, and with intermediaries in $NO_x$ formation. Reaction of these species with CaO to form solid products such as $CaCN_2$ will reduce the overall gas-phase concentration of nitrogen species. This effect, in turn, will reduce the overall concentration of nitrogen species in the exit gas although the relative distribution of $N_2$, $NH_3$, HCN, and NO is expected to remain largely unchanged. Unfortunately, no experimental data are available at the present time to substantiate these effects. This situation could be remedied by conducting small-scale experiments with CaO and representative gases under gasifier conditions and/or by modeling the CaO interactions with a validated reaction model.

## 5.2 EFFECT OF CALCIUM OXIDE ON FUEL SULFUR-DERIVED POLLUTANTS

The fuel sulfur-derived pollutants in an entrained-bed slagging gasifier may be generated from organic, elemental, or inorganic sulfur compounds present in the feed coal. The pyrolysis of coal in the fuel rich reducing atmosphere leads to devolatilization of sulfur compounds which readily are reduced to produce $H_2S$. The devolatilization reactions include:

$$FeS_2 \longrightarrow FeS + 1/2\ S_2 \xrightarrow{H_2} H_2S + FeS \qquad (5\text{-}5)$$

$$R\text{-}S\text{-}R' \xrightarrow{H_2} H_2S + \text{----} \qquad (5\text{-}6)$$

$$S \xrightarrow{H_2} H_2S + \text{----} \qquad (5\text{-}7)$$

and are considered very fast under the gasifier temperature and pressure conditions. This situation is more or less comparable to the generation of HCN discussed in reaction (5-1). The overall devolatilization reaction of hydrosulfurization may be considered to occur at infinite rate.

As has been discussed before, some of the sulfur is also released as $SO_2$ in the gas phase.[3] This has been confirmed by the Battelle data generated by reacting CaO with iron pyrites in a nitrogen atmosphere.[8] In the analytical study of the effluents from a high temperature entrained flow gasifier by Hansen, et al.,[9] the presence of $SO_2$ has not been measured in the product gases from the gasifier. However, the product gas analyzed was scrubbed by water before sampling. Personal communication[10] indicates that the absence of $SO_2$ in the product gas may be due to water absorption of the product. Also, COS, $CS_2$, NO, $NH_3$, or amines were not encountered in the product stream in this study. $H_2S$, HCN, and molecular nitrogen were reported in the product gases.

Attar[10] in his review paper mentions the presence of COS and $CS_2$ in the gasifier. COS and $CS_2$ are formed in the gasifier due to the reactions of devolatilized sulfur in the gas phase with carbon and the reaction of product $H_2S$ with carbon dioxide.

$$CO_2 + H_2S \rightleftharpoons COS + H_2O \tag{5-8}$$

$$COS + H_2S \longrightarrow CS_2 + H_2O \tag{5-9}$$

$$C + S_2 \longrightarrow CS_2 \tag{5-10}$$

The above discussion suggests that for an effective in-process control of the sulfur pollutants by capture of sulfur in the slag, the sorbent added should be capable of reacting with the major sulfur species like COS and $H_2S$. Under other gasification conditions, lime has been used extensively as scavenger of $H_2S$ and $SO_2$. Considerable information on the reactions of CaO and $H_2S$ and CaO and $SO_2$ is available from LIMB studies[1,8] and other experimental studies. The basic reactions of CaO with various sulfur-intermediates in the reducing atmosphere of a gasifier may be

$$H_2S + CaO \longrightarrow CaS + H_2O \tag{5-11}$$

$$COS + CaO \longrightarrow CaS + CO_2 \tag{5-12}$$

$$S_2 + CaO \longrightarrow CaS + SO \qquad (5\text{-}13)$$

$$3SO \longrightarrow S_2O + SO_2 \qquad (5\text{-}14)$$

Table 5-1 summarizes some of the reactions studied under the LIMB program.[8] Calcium oxide will react directly with $SO_2$ to form $CaSO_3$

$$CaO + SO_2 \rightleftharpoons CaSO_3 \qquad (5\text{-}15)$$

$$CaO + SO_2 + \frac{1}{2} O_2 \rightleftharpoons CaSO_4 \qquad (5\text{-}16)$$

One report[11] provides a host of thermochemical information on these reactions.

The equilibria of $H_2S$ absorption may be represented by the reaction

$$CaO + H_2S \rightleftharpoons CaS + H_2O \qquad (5\text{-}11)$$

Calcium oxide will react with $H_2S$ to give only one calcium sulfide since no other sulfides are possible with calcium[11]. This equilibrium reaction has been extensively studied by Rosenqvist[11a] and by Sander and Healy.[11b] The most recent information providing insight into various reactions occurring in the fuel-rich reducing zone of staged combustion is presented by Levy, et al.[8] The rate constants for the reactions studied are presented in Table 5-1. Of particular interest are the Reactions 5, 6, 7 and 8. Comparison of Reactions 6 and 7 indicates that the rate constant of Reaction 5-11 is not significantly affected by the presence of a large quantity of hydrogen in the reaction atmosphere. This would suggest that the rate constants for Reactions 5, 6 and 8 will represent the rate constants for reactions of CaO and $H_2S$ at these given temperatures. An Arrhenius plot for the reaction based on the data in Table 5-1 is presented in Figure 5-1. It is apparent from the Arrhenius plot that the rate constant decreases significantly from 1242 K to 1373 K. On the basis of thermodynamic

## TABLE 5-1. RATE CONSTANTS FOR STUDIED REACTIONS OF CaO WITH COS and $H_2S$

| Experiments | Reaction | Temp, (°C) | k, ($sec^{-1}$) |
|---|---|---|---|
| | COS | | |
| 1 | $CaO + COS + CO \longrightarrow CaS + CO_2 + CO$ | 871 | $1.06 \times 10^{-3}$ |
| 2 | $CaO + COS + CO \longrightarrow CaS + CO_2 + CO$ | 969 | $1.16 \times 10^{-3}$ |
| 3 | $CaO + COS \longrightarrow CaS + CO_2$ | 973 | $9.62 \times 10^{-4}$ |
| 4 | $CaO + COS + CO \longrightarrow CaS + CO_2 + CO$ | 1079 | $1.23 \times 10^{-3}$ |
| | $H_2S$ | | |
| 5 | $CaO + H_2S + H_2 \longrightarrow CaS + H_2 + H_2O$ | 864 | $9.19 \times 10^{-4}$ |
| 6 | $CaO + H_2S + H_2 \longrightarrow CaS + H_2 + H_2O$ | 969 | $6.34 \times 10^{-3}$ |
| 7 | $CaO + H_2S \longrightarrow CaS + H_2O$ | 969 | $6.88 \times 10^{-3}$ |
| 8 | $CaO + H_2S + H_2 \longrightarrow CaS + H_2 + H_2O$ | 1100 | $4.31 \times 10^{-3}$ |

Note: CO concentration in Experiments 1, 2, and 4 is 11.5 percent, 0 percent in Experiment 3. $H_2$ concentration in Experiments 5, 6, and 8 is 16.7 percent, 0 percent in Experiment 7. (Reference 8)

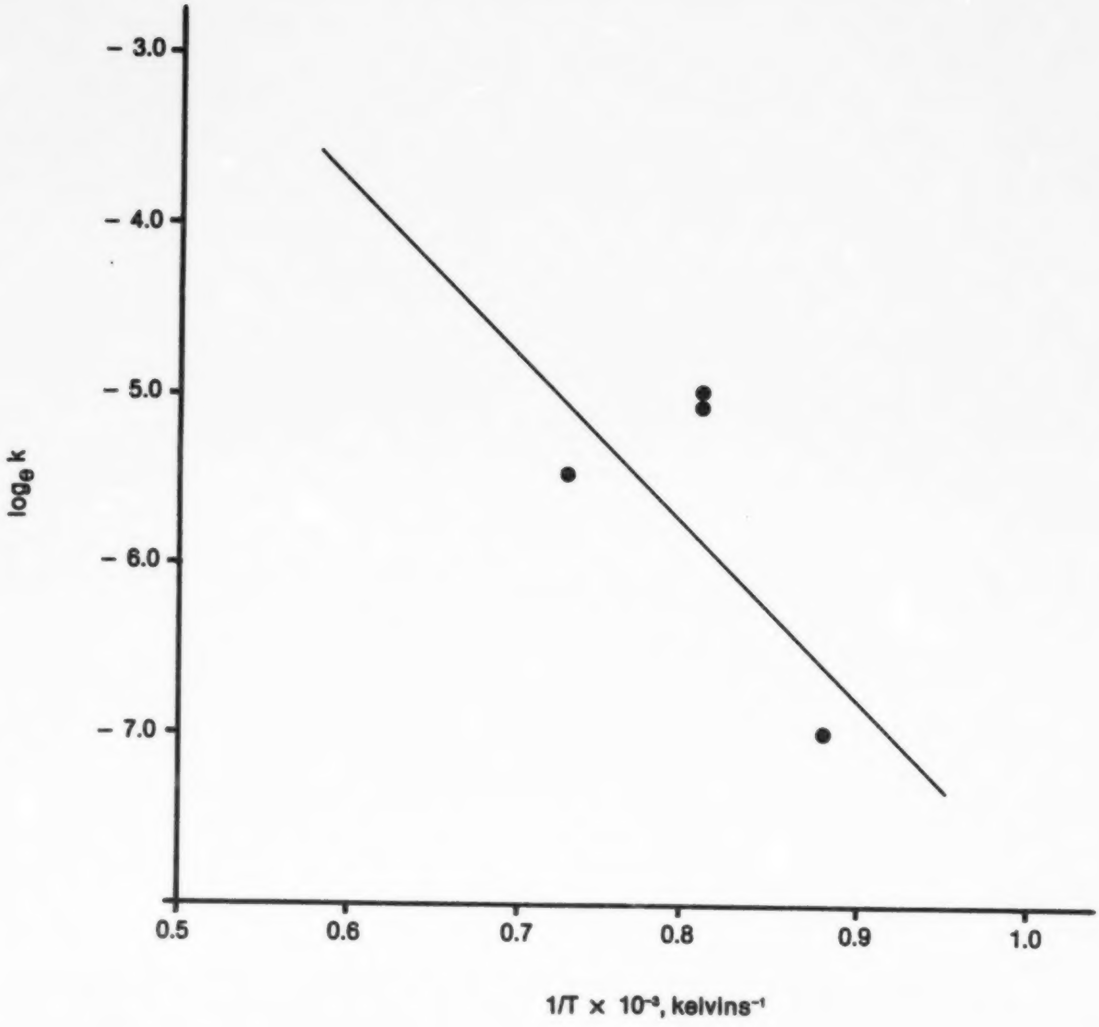


Figure 5-1. Arrhenius plot of the CaO + $H_2S$ reactions from Table 5-1.

considerations one would expect a higher rate constant value at 1373 K than at 1242 K. However, it is known that various other physical and chemical factors come into play which can influence this reaction greatly.

The principal variables that determine the rate of $H_2S$ capture are reaction temperature, specific surface area of CaO, and $SO_2/H_2S$ partial pressures[1a]. The most applicable study of the sulfur capture reactions under gasifier conditions was conducted by H. Freund.[12,13] Freund demonstrated that

$$CaO + H_2S \rightleftharpoons CaS + H_2O \qquad (5\text{-}11)$$

is the principal sulfur capture reaction with an activation energy of 23 Kcal/mole. In the temperature region of 1,065 to 1,310°C, the absorption reaction of $H_2S$ is first order with respect to calcium oxide and half order with respect to $H_2S$. An extrapolation of the Arrhenius plot of the CaO + $H_2S$ reaction in Figure 5-1 suggests (from a linear regression) a $\log_e$ K value of about -5.0, or a K value of about $6.32 \times 10^{-3}$ at 1,373 K. The experimental value given in Table 5-1 is $4.31 \times 10^{-3}$, or about 47 percent lower. This may reflect the magnitude of the random error for this kind of experiment, or it may suggest that a different reaction (and equilibrium) mechanism is at work at 1,373 K.

The possible explanation for this dependence of rate constants on temperatures is presented in the thermodynamics discussion of a Battelle Energy Program Report entitled "The Superslagging Gasifier - Demonstration of Desulfurizing Principle."[11a] Normally, the equilibrium constant for Reaction 5-11 is expressed as

$$K = \frac{a_{CaS} P_{H_2O}}{a_{CaO} P_{H_2S}}$$

where the activity of CaS and CaO is usually considered as 1. However, it is known that the chemical activity of a reactant may vary from 1 for the pure compound down to 0 when the compound is in the dilute form. The activity is also known to change with a change in crystal structure, physical changes in the surface such as due to sintering, or solution of one compound in another. The solubility of CaS in the slag depends on the composition of the slag which, in turn, depends on the source of coal. The solubility data for CaS in the lime-alumina-silica system indicate nearly 10 percent CaS solubility in $CaO-SiO_2$ melts. Any considerable desulfurization will result in high CaS levels in slag and therefore it is reasonable to assume that solid CaS will be present at equilibrium. Under these conditions CaS activity may be considered as 1.

For calcium oxide activity, though, one cannot assume the value of 1, even if a large excess is used. The sintering phenomenon accompanied by changes in the crystal structure assume significant importance at high temperatures. The reaction has been proven to be a diffusion controlled reaction. According to Freund[12], the $H_2S$ adsorption reaction is not controlled by mass transfer between the particles and the gas stream. Freund found that at higher temperatures, the sintering or desurfacing process seems to win over the $H_2S$ absorption reaction evidenced by the reaction rate falling off considerably at 1310°C compared to 1065°C. Equilibrium calculations indicate that at 1065°C, 99.1 percent of the sulfur is present as CaS whereas at 1310°C only 95.8 percent sulfur is converted to CaS. The set of data on sulfur capture does not indicate any correlation with the temperature, particle size of lime, or other particle-associated parameters. The rate-limiting step appears to be the intraparticle diffusion process. Although diffusion itself is not a strongly temperature dependent phenomenon, desurfacing will have a dramatic effect on the diffusion rate. Unless a rate constant for the entire desurfacing phenomenon (including sintering, diffusion inhibition, etc.) and its temperature and particle size dependence are known, it will be very difficult to estimate the kinetic rates at the gasification conditions.

It may be possible to estimate the equilibrium concentration of $H_2S$ at gasifier conditions using the information in Figure 5-2. Table 2-5 of this report presents raw gas minor constituents for oxygen-blown gasifier

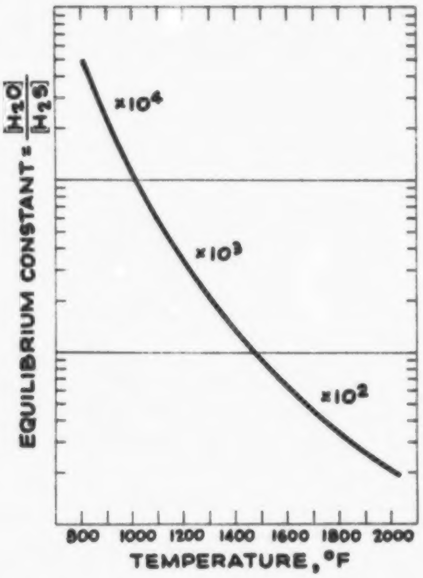


Figure 5-2. Equilibrium constant for the reaction:

$CaO + H_2S \longrightarrow CaS + H_2O.$[14]

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operation. The typical $H_2S$ concentration is reported in the range of 1.11 to 1.90 mole percent, on a dry basis. For the purposes of estimating the limiting equilibrium concentrations of $H_2S$, the upper limit of concentration is assumed. Since the $H_2S$ concentration represents the devolatalized sulfur species it may be assumed that $H_2S$ concentration will be independent of the gasifier temperature after complete devolatilization has occurred. It has already been noted that sulfur devolatilization to $H_2S$ will be complete well before coal reaches the temperatures of 800 to 1,000°C

Using the equilibrium constant data for the reaction

$$H_2S + CaO \rightleftharpoons H_2O + CaS \tag{5-11}$$

from Figure 5-2, and the initial concentration of $H_2S$ is 0.019 mole per mole of gas, it is possible to calculate the concentration of $H_2S$ at different temperatures

$$K = \frac{[CaS]\,[H_2O]}{[CaO]\,[H_2S]} , \tag{5-17}$$

or

$$K \simeq \frac{[H_2O]}{[H_2S]} . \tag{5-18}$$

Initially, when CaO is in contact with $H_2S$, the concentration of water is near zero and $H_2S$ concentration is 0.019 mole per mole of gas. If x moles of $H_2S$ react with CaO, then

$$[H_2S] = (0.019 - x) ,$$
$$[H_2O] = x .$$

From Figure 5-2, the equilibrim constant at 1100°C is approximately 200, or

$$K = 200 = \frac{x}{0.019 - x}, \qquad (5\text{-}19)$$

and $x = 0.0189$ .

Hence, at equilibrium, 99.5 percent of the initial $H_2S$ is converted to CaS and the residual $H_2S$ concentration at 1100°C is about 0.01 mole percent. From an equilibrium standpoint, therefore, the capture of $H_2S$ by CaO at these temperatures is highly favored.

Although the reaction of $H_2S$ with CaO to yield CaS is heavily favored at equilibrium under conditions that would exist near the outlet of the gasifier (i.e., in the lower temperature regions), the equilibrium data discussed above cannot predict the extent to which equilibrium will be achieved. To do so, one must consider kinetic data which indicate the rate at which the reactions will proceed toward equilibrium. Freund conducted laboratory experiments to determine the intrinsic global rate constant for the high-temperature reaction of CaO with $H_2S$.[12,13] This rate constant accounts for both the rate of the chemical reaction as well as the effects of pore diffusion. Although the experiments were conducted with CaO-impregnated amorphous carbon, the results should also be applicable to calcium-containing char and CaO in general if the surface area at reaction conditions can be adequately determined. The data were analyzed with the expression:

$$\frac{dX}{dt} = k\,(1 - X)\,Cg, \qquad (5\text{-}20)$$

where X is the fractional conversion of CaO to CaS, k is the intrinsic rate constant, and Cg is the $H_2S$ gas concentration. In the experimental procedure, the solid particles were fed from the top of an entrained flow reactor at a rate slow enough that little change in $H_2S$ concentration was observed. In an actual entrained flow gasifier, however, Cg will change markedly if $H_2S$ capture by CaO is significant and cannot be assumed to be a constant as in Equation 5-20. It can be shown that the concentration of $H_2S$ at any time, $Cg_t$, is given by:

$$Cg_t = Cg_i (1 - X \cdot RR), \qquad (5\text{-}21)$$

where $Cg_i$ is the initial $H_2S$ concentration before reactions begin and RR is the reagent ratio or molar ratio of injected CaO to $H_2S$. Substituting this expression into Equation 5-20 yields:

$$\frac{dX}{dt} = kCg_i(1 - X)(1 - X \cdot RR) \qquad (5\text{-}22)$$

and

$$\frac{dX}{(1-X)(1-X \cdot RR)} = k\ Cg_i\ dt \qquad (5\text{-}23)$$

Integration of this equation between the limits of $X = 0$ at $t = 0$ and $X = X_f$ at $t = t_f$ yields

$$\frac{1}{(1-RR)} \ln \left(\frac{1 - RR \cdot X_f}{1 - X_f}\right) = k\ Cg_i\ t_f \qquad (5\text{-}24)$$

This equation relates the time required for a given factional conversion of CaO to the reagent ratio, rate constant, and initial $H_2S$ concentration.

Freund derived intrinsic global rate constants for the CaO - $H_2S$ reaction between temperatures of 1,400°K and 1,700°K and for $H_2S$ concentrations between 2.66 and 3.24 $g/cm^3$.

At a temperature of 1,500°K (or 1,227°C), the intrinsic global rate constant was found to be $2.371 \times 10^6$ $cm^3$/sec-g based on CaO surface area of 28 $m^2$/g. For a gas containing 1,900 ppm of $H_2S$ at 600 psig and 1,500°K, $Cg_i$ equals $2.168 \times 10^{-5}$ $g/cm^3$. Assuming that CaO is injected at this temperature into an entrained bed gasifier at a reagent ratio of 3.0 (and ignoring the heat of reaction and other heat effects), Equation 5-24 predicts that 50 percent of the $H_2S$ will be converted to CaS in 0.00497 seconds. For the same example, 95 percent of $H_2S$ will be converted within 0.0254 seconds.

These reaction times are much shorter than the residence times which are typical of entrained-bed gasifiers (i.e., a second or more). When combined with the thermodynamic analyses, these results indicate that the $CaO$ - $H_2S$ reaction should proceed significantly toward completion within the gasifier. However, the only operating data available on sulfur capture by CaO in a gasifier were reported by TRW for their pre-combustor system and indicate 40 to 60 percent $H_2S$ capture. The most likely reason for this difference between actual and experimental results is that the CaO surface area in the TRW gasifier/combuster was significantly lower than that used by Freund in his experiments. The higher temperatures of the TRW system could well have led to sintering and desurfacing of injected CaO, thus reducing the effective surface area available for reaction with $H_2S$. This speculation is supported by the data in Figure 5-1 which indicate that the reaction rate reaches a maximum near 970°C and then declines at 1,100°C.

If CaO is injected at temperatures below sintering temperatures, kinetic and thermodynamic analyses indicate that reaction with $H_2S$ to form CaS should proceed rapidly to completion. Although kinetic data are not available for the reactions of CaO with COS or $CS_2$, it is likely that these reactions will also be rapid given the chemical similarity of gaseous $H_2S$, COS, and $CS_2$.

These observations suggest that CaO should be added to the gasifier at lower temperatures to avoid desurfacing effects. However, the coal conversion requirements for an efficient gasifier demand that it be operated at higher temperatures. A possible compromise for maximum absorption activity and minimum desurfacing activity for lime may be to add lime in the regions of lower temperature away from the flame. Probably a staged addition of lime will have to be adopted to facilitate removal of $NO_x$ and $SO_x$ precursors. Part of the CaO may be added with the coal slurry to capture $H_2S$/HCN released by initial devolatilization (producing primarily $CaCN_2$), but the major portion of the lime may be added in the temperature regions of 800 to 1,000°C. The optimum position for the addition of CaO will, of course, depend on the reactor design and flow conditions.

As has been discussed in Sections 2.3 and 2.4, the major components of the raw product gas are hydrogen, carbon dioxide, and carbon monoxide. Some minor components encountered in this stream for an oxygen blown gasifier operation are included in Table 2-5. In the interest of estimating the effectiveness of the in-process removal of sulfur compounds during gasification it will be necessary to consider the effect of hydrogen, carbon dioxide, and carbon monoxide on the reaction

$$CaO + H_2S \rightleftharpoons CaS + H_2O \qquad (5\text{-}11)$$

or the products formed therein. The Arrhenius plot for the reaction in Figure 5-1 and corresponding discussion suggest that large amounts of hydrogen in the gasifier atmosphere will have no significant effects on the rates of sulfur capture. The major $CO/CO_2$ reaction with calcium oxide leads to the formation of calcium carbonate

$$CaO + CO_2 \rightleftharpoons CaCO_3 \qquad (5\text{-}25)$$

However at high temperatures, such as those expected in an entrained-bed gasifier, the equilibrium is far toward the left and any carbonate formed will decompose back to calcium oxide. The $CO_2$ Acceptor process as developed by Conoco Coal Development Company is largely based on this concept.[14] According to Curran, et al., the literature data imply that equilibrium $CO_2$ pressure depends on the origin of the calcium carbonate. Their experimental measurements, however, indicated that the equilibrium $CO_2$ pressure is independent of all conditions except temperature. The reactions and the kinetics or rate constants for these reactions are included in Table 5-2.

The reactions in Table 5-2 indicate that conditions should be maintained so that both CaS and $CaSO_4$ can coexist without releasing $SO_2$ via Reaction 3 listed in the table. Experimentally, Curran, et al., found that complete sulfur rejection was always obtained from the acceptor. Favorable

## TABLE 5-2. EQUILIBRIUM CONSTANTS FOR REACTIONS OF $CaCO_3$, CaS, and $CaSO_4$[a]

| Reaction | Kp° at °F* | | |
|---|---|---|---|
| | 1800 | 1900 | 1950 |
| 1. $CaCO_3 = CaO + CO_2$ | 3.14 | 6.01 | 8.12 |
| 2. $CaS + H_2O = CaO + H_2S$ | 0.0025 | 0.0032 | 0.0036 |
| 3. $3/4\ CaSO_4 + 1/4\ CaS = CaO + SO_2$ | 0.042 | 0.113 | 0.182 |
| 4. $1/4\ CaS + H_2O = 1/4\ CaSO_4 + H_2$ | 0.0100 | 0.0105 | 0.0109 |
| 5. $1/4\ CaS + CO_2 = 1/4\ CaSO_4 + CO$ | 0.0166 | 0.0200 | 0.0218 |
| 6. $CaS + CO_2 = CaO + COS$ | 0.00022 | 0.00031 | 0.00037 |
| 7. $1/2\ CaSO_4 + 3/2\ CaS = 2CaO + S_2$ | 0.00031 | 0.00096 | 0.00163 |

* Kp° is either dimensionless or expressed in atmospheres.

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[a] Source: Curran, et al., $CO_2$ Acceptor Process, in Fuel Gasification, Advances in Chemistry Series #69, American Chemical Society, Washington, D.C., 1967.

conditions could be obtained in experiments using no air so that only Reactions 5 and 3 in Table 5-2 occurred in succession. Sulfur rejection was also observed when excess air was used by Curran, et al., in the regenerator in apparent violation of the equilibrium in dissociation of the sulfate. This may be due to existence of reducing conditions in the $CO_2$ Acceptor process gasifier bed. In the entrained bed gasifier the existence of highly reducing atmosphere will indeed allow sulfur to be rejected by Reaction 3 in Table 5-2.

## 5.3 REMOVAL OF THE FUEL-N AND FUEL-S DERIVED POLLUTANTS

It is expected that the sulfur and nitrogen compounds captured by the added calcium oxide will be removed from the reactor with the slag when dry heat recovery is used. The calcium sulfide formed in the slag may have RCRA hazardous characteristics such that CaS may release toxic $H_2S$ under disposal conditions when it comes in contact with acid or water. The most desirable option will be to convert the calcium sulfide formed to calcium sulfate by oxidation or by a reaction such as

$$CaS + 4CO_2 = CaSO_4 + CO \qquad (5\text{-}26)$$

Calcium sulfide itself will readily undergo decomposition in the presence of water or water and $CO_2$.

$$S^- + H_2O \rightleftharpoons HS^- + OH^- \qquad (5\text{-}27)$$

$$HS^- + H_2O \rightleftharpoons H_2S + OH^- \qquad (5\text{-}28)$$

$$CaS + H_2O + CO_2 \rightleftharpoons CaCO_3 + H_2S \qquad (5\text{-}29)$$

$$\frac{1}{4}\,CaS + H_2O \rightleftharpoons CaSO_4 + H_2 \qquad (5\text{-}30)$$

Reactions 5-27 and 5-28 indicate the mechanism for hydrolysis of calcium sulfide. The review of these reactions suggests the possibility of re-release of $H_2S$ from the slag in the gasifier if the slag is quenched inside the gasifier. The temperature dependence of the major reactions is presented in Figures 5-1, 5-2, 5-3, and 5-4. The process of cooling the slag by dropping it in water, as is done in the quench chamber of some of the slagging gasifiers, may have to be modified when calcium oxide is used in the gasifier. A design to exploit reactions (5-24) and (5-28) to generate combustible gases and innocuous calcium sulfate, which can be safely disposed of, is desirable.

## 5.4 OTHER SORBENTS FOR IN-PROCESS CONTROL OF $SO_x$ and $NO_x$

The Department of Energy is developing a process in which copper oxide is used in a fluidized bed process for removal of $SO_x$ and $NO_x$. The technique is being developed as a post gasification scrubber or a scrubber for flue gases.[15] The copper oxide absorbs sulfur from the flue gases at 400°C. Ammonia is injected into the combustion gases. Ammonia reacts with nitrogen oxides to produce nitrogen gas and water. Application of copper oxide to the entrained bed gasifier in-process control situation has not been considered.

High temperature desulfurization/regeneration reactions of metal oxides studied under the Fuel Cell Program at Argonne National Laboratories may also suggest some feasible sorbents such as $V_2O_5/V_2O_3$, $WO_3/WO_5$ and CuO/Cu systems. They have also considered the sulfur uptake of ZnO, $Cr_2O_3$, $BaCO_3$ and $SrCO_3$.

It is suggested that other sources of alkaline material could be used to scavenge sulfur compounds at gasifier temperatures and may be economical or commercially viable. The alkaline dust from the cement manufacturing industry or the alkaline fly ash from utility boilers are likely candidate sorbents. Both the sources are plentiful, are distributed throughout all regions of the United States, and create an environmental problem due to the generation of alkaline leachate when stored as a pile or landfill.

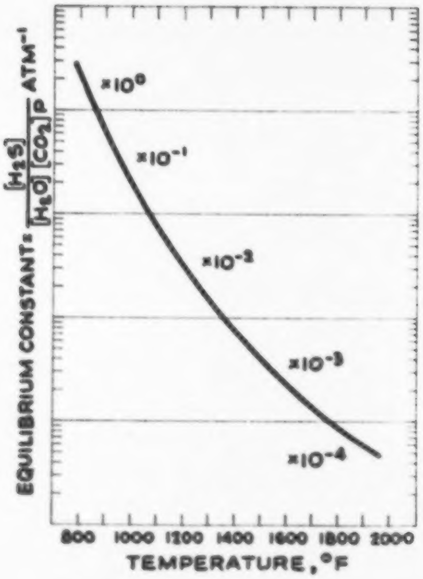

Figure 5-3. Equilibrium constant for the reaction:
$CaS + H_2O + CO_2 \longrightarrow CaCO_3 + H_2S.$[14]

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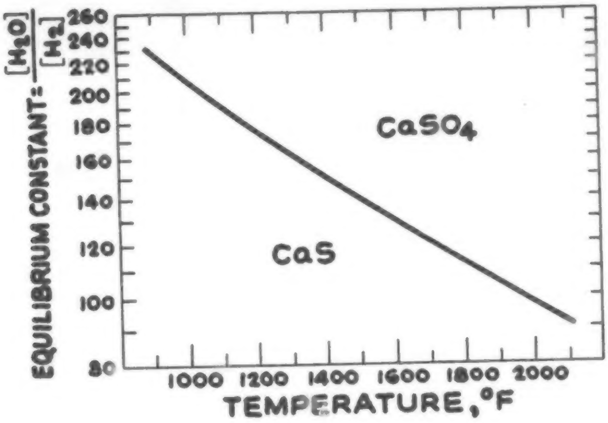

Figure 5-4. Rough estimate of equilibrium constant for:

$$CaSO_4 + 4H_2 \longrightarrow CaS + 4H_2O.^{14}$$

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Moreover, the particle size of the sorbents is desirably small for better adsorption properties.

Flue gas desulfurization technology employs an alkali as a sorbent for removal of $SO_2$ at low temperatures. The amount of sulfur retained by fly ash has been correlated with the levels of alkaline metal oxides (CaO, $Na_2O$, MgO and $K_2O$) contained within the ash.[18] Further, it was found that decreasing particle sizes exhibited an increase in the sulfur capture by the ash product suggesting a specific surface area-related phenomenon. Tables 5-3, 5-4, and 5-5 summarize the characterization information on fly ash under flue gas desulfurization (FGD) conditions. The information on the use of fly ash in the highly reducing slagging entrained-bed gasifier is not available. It is expected that the metal oxides will be very efficient in the removal of $SO_2$, $H_2S$, COS, and HCN intermediates from the product gases. In addition to the reactions of CaO discussed in this section, high temperature and pressure reactions of "other" metal oxides and their sulfur scavenging properties will play a significant role in the in-process control of $SO_x$ and $NO_x$ in the entrained-bed gasifier. It is expected that the diffusion properties, based on calcination temperature, porosity and surface area will be remarkably different for fly ash samples than from calcium oxide alone. The conversion of CaS to $CaSO_4$ releasing sulfur in secondary reaction

$$CaS \xrightarrow{O_2} \frac{1}{4}\,CaS + \frac{3}{4}\,CaSO_4 \longrightarrow CaSO_4 \overset{O_2}{\rightleftharpoons} SO_2 + CaO \qquad (5\text{-}31)$$

will be dissimilar for other metal sulfides and one may not be able to generalize the reaction as:

$$MS + O_2 \longrightarrow MO + SO_2 \qquad (5\text{-}32)$$

Table 5-6 indicates that magnesium, iron, or sodium sulfides formed will be stable compared with calcium sulfide. The formation of calcium

## TABLE 5-3. SUMMARY OF FLY ASH CHEMICAL CHARACTERISTICS

| Fly Ash Identification No. | % S | % CaO | % $Na_2O$ | % MgO | % $K_2O$ | TAMO[a] |
|---|---|---|---|---|---|---|
| | | | Lignite | | | |
| 27 | 0.66 | 14.99 | 11.19 | 2.40 | 1.70 | 28.33 |
| 38C | 0.00 | 13.95 | 35.88 | 5.58 | 3.69 | 56.47 |
| 41 | 4.06 | 18.01 | 16.68 | 3.98 | 1.52 | 32.47 |
| 42 | 1.02 | 18.96 | 10.97 | 3.79 | 1.90 | 33.67 |
| 44 | 0.75 | 23.80 | 17.71 | 4.57 | 1.14 | 45.56 |
| | | | Subbituminous | | | |
| 13 | 0.49 | 13.96 | 10.96 | 2.79 | 1.79 | 28.06 |
| 14 | 0.73 | 22.91 | 10.96 | 3.49 | 1.29 | 38.22 |
| 18A | 0.70 | 18.96 | 10.78 | 3.79 | 1.50 | 33.73 |
| 37 | 0.78 | 24.95 | 10.98 | 3.59 | 1.00 | 39.19 |
| 38B | 0.72 | 21.81 | 13.48 | 2.97 | 1.29 | 37.70 |
| 43 | 0.66 | 6.97 | 10.76 | 1.00 | 2.49 | 18.50 |
| 45 | 0.68 | 11.63 | 10.66 | 2.71 | 1.45 | 24.68 |
| 46 | 0.75 | 28.90 | 14.94 | 3.98 | 1.39 | 47.47 |
| | | | Bituminous | | | |
| 6 | 0.43 | 7.79 | 10.71 | 0.97 | 2.53 | 19.61 |
| 10 | 0.32 | 5.44 | 9.42 | 0.91 | 2.36 | 16.03 |
| 18B | 0.45 | 9.72 | 10.89 | 2.14 | 1.94 | 22.83 |
| 23B | 1.87 | 7.88 | 10.25 | 1.18 | 1.68 | 16.54 |
| 24 | 1.22 | 8.60 | 9.94 | 1.91 | 0.76 | 17.67 |
| 34 | 1.04 | 6.76 | 11.79 | 0.97 | 2.90 | 18.78 |
| 36 | 0.36 | 0.98 | 12.69 | 0.39 | 5.56 | 15.75 |
| 49 | 2.19 | 4.02 | 6.97 | 0.94 | 1.94 | 8.89 |
| 50 | 0.41 | 5.75 | 12.47 | 1.44 | 2.78 | 20.01 |

[a] Total alkaline metal oxides reported in g/100 g as CaO.

## TABLE 5-4. SUMMARY OF SLURRY AND FILTRATE ALKALINITY SPECIES[a]

| Coal Sample No. | Slurry | | | | Filtrate Total |
|---|---|---|---|---|---|
| | OH | $CO_3$ | $HCO_3$ | Total | |
| | | Lignite | | | |
| 27 | 0 | 2141 | 428 | 2569 | 1700 |
| 38C | 1713 | 3854 | 0 | 5567 | 1600 |
| 41 | 0 | 8135 | 7065 | 15200 | 1100 |
| 42 | 0 | 8564 | 1285 | 9849 | 3700 |
| 44 | 0 | 16701 | 8350 | 25051 | 1300 |
| | | Subbituminous | | | |
| 13 | 4496 | 3425 | 0 | 7921 | 3800 |
| 14 | 6637 | 3854 | 0 | 10491 | 2500 |
| 18A | 3426 | 0 | 0 | 3426 | 1200 |
| 37 | 5352 | 13702 | 0 | 19054 | 1800 |
| 38B | 642 | 5139 | 0 | 5781 | 1500 |
| 43 | 3426 | 8564 | 0 | 11990 | 2100 |
| 45 | 0 | 3854 | 1070 | 4924 | 1600 |
| 46 | 0 | 5566 | 2569 | 8135 | 1600 |
| | | Bituminous | | | |
| 6 | 0 | 0 | 0 | 0 | 200 |
| 10 | 0 | 0 | 8564 | 8564 | 500 |
| 18B | 1285 | 5995 | 0 | 7280 | 3400 |
| 23B | 2783 | 0 | 0 | 2783 | 1800 |
| 24 | 1285 | 3426 | 0 | 4711 | 2900 |
| 34 | 0 | 0 | 0 | 0 | 0 |
| 36 | 2141 | 0 | 0 | 2141 | 1400 |
| 49 | 0 | 0 | 0 | 0 | 0 |
| 50 | 0 | 0 | 0 | 0 | 0 |
| 30A | 0 | 0 | 0 | 0 | |

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[a] All values are mg/L as $CaCO_3$.

## TABLE 5-5. SULFUR RETENTION BY FLY ASH

| Fly Ash Identification No. | $SO_2$ Removal, Percent | |
|---|---|---|
| | Spray Dryer | Total (System) |
| | **Lignite** | |
| 27 | 1 | 5 |
| 38C | 11 | 15 |
| 41 | 17 | 21 |
| 42 | 8 | 9 |
| 44 | 15 | 16 |
| | **Subbituminous** | |
| 13 | 5 | 17 |
| 14 | 33 | 30 |
| 18A | 20 | 21 |
| 37 | 25 | 26 |
| 38B | 17 | 26 |
| 43 | 21 | 26 |
| 45 | 11 | 24 |
| 46 | 12 | 13 |
| | **Bituminous** | |
| 6 | 0 | 1 |
| 10 | 10 | 7 |
| 18B | 24 | 23 |
| 23B | 2 | 2 |
| 24 | 5 | 6 |
| 34 | 5 | 6 |
| 36 | 0 | 0 |
| 49 | 11 | 29 |
| 50 | 0 | 1 |

### TABLE 5-6. MELTING POINT RANGES FOR METAL OXIDES IN DEGREES CENTIGRADE

| | Oxide | Sulfide | Sulfate | Cyanide | Cyanamid |
|---|---|---|---|---|---|
| Magnesium | 2800 | d 2000 | d 1124 | Mg $(CN)_2$ to $MgCN_2$ at 300 | d 600 |
| Calcium | 2500 to 2850 | d | 1450 | d 350 | sub 1350 |
| Iron | 1538 | 1193 to 1199 | -- | Various (d) | d |
| Potassium | 350 to 490 | Various Form 145 to 840 | 1069 | 635 | -- |
| Sodium | sub 1275 | 1180 | 34 to 884 | 563 to 1496 | -- |

Source: CRC Handbook of Chemistry and Physics, 49th Edition, The Chemical Rubber Co., Ohio, (1968-67).

d = decomposes; sub = sublimes

sulfide and the oxidation of calcium sulfide resulting in the formation of calcium sulfate has been discussed extensively in the literature connected with LIMB technology.[1] It appears that the use of alkaline fly ash as scavenger for $H_2S$, $SO_2$ and COS, HCN, and $NO_x$ under the entrained-bed gasifier condition merits some attention.

Another commercially viable sorbent for the gasification may be the highly alkaline cement kiln dust which is usually too alkaline to be recycled as the product. Approximately 12 percent of the kiln feed exits from the kiln with the gas upstream of any air pollution control device. As of 1975, about 16.4 million tons of alkaline dust was collected annually. Of this, EPA estimates that 27 percent is discarded in some manner, usually as waste piles.

Collected kiln dust has a wide particle size range as shown in Table 5-7. Over 90 percent of the dust particles are less than 12 microns in diameter. Table 5-7 shows the concentration distribution of alkalies collected from electrostatic precipitators. The alkali content of the kiln dust is the most important factor that determines whether the dust can be recycled to low alkaline cement production. Tables 5-8 and 5-9 are included to indicate the types of metal oxides that may be present in the dust. Cement manufacturing processes use (different) locally available materials (sources of lime and coal) that vary in composition. By suitable adjustments to kiln processes, they produce a uniform product within certain specifications. Hence, the kiln dust composition can vary from source to source. Radian Corporation's experience in commercial analysis of these dust indicates that usually the cement dust has alkalinity equivalent of 35-40 percent, expressed as sodium oxide.[19] In addition to these oxides, the kiln dust also seems to contain various heavy metals which may form several stable salts or complexes with sulfur and nitrogen intermediates which may be rejected with the slag.

The reactions of all these metal oxides and salts with the product components such as $H_2S$, $CO_2$, COS, $NO_2$, NO, HCN, $SO_2$, etc., are very complex. Of particular interest is the ability of the heavy metals to form compounds

TABLE 5-7. PARTICLE SIZE ANALYSIS[a] AND DISTRIBUTION ALKALIES IN A SPECIMEN KILN DUST[b]

| Range (Microns) | Weight Percent | Total Alkalies Percent | | Water Soluble Alkalies Percent | | Water Insoluble Alkalies Percent |
|---|---|---|---|---|---|---|
| | | $Na_2O$ | $K_2O$ | $Na_2O$ | $K_2O$ | $K_2O$ |
| +68 | 0 | - | - | - | - | - |
| 68-48 | 0.3 | 0.30 | 3.62 | -[c] | -[c] | - |
| 48-34 | 0.4 | 0.31 | 3.46 | -[c] | -[c] | - |
| 34-24 | 0.7 | 0.35 | 4.51 | 0.094 | 1.927 | 2.58 |
| 24-17 | 1.8 | 0.38 | 5.08 | 0.117 | 2.560 | 2.52 |
| 17-12 | 5.1 | 0.40 | 5.15 | 0.134 | 3.072 | 2.08 |
| 12-6 | 27.3 | 0.33 | 5.35 | 0.134 | 3.252 | 2.10 |
| -6 | 64.4 | 0.42 | 10.72 | 0.242 | 8.191 | 2.53 |

[a] Particle size analysis was carried out by the Allis-Chalmers Corporation using an "infrasizer" particle size analyzer.

[b] Low chloride precipitator kiln dust cf. Table 18, No. 2.

[c] Insufficient sample for analysis.

Source: Greening, N. R., F. M. Miller, C. H. Weise, and H. Nagao, Elimination of Water Pollution by Recycling Cement Plant Kiln Dust, EPA-600/2-76-194, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1976. 69 pp.

## TABLE 5-8. DRY KILN DUST ANALYSIS[a]

| | | Concentration, Weight, Percent |
|---|---|---|
| Cations | | |
| Lithium | (Li) | 0.0064 |
| Sodium | (Na) | 12.25 |
| Potassium | (K) | 24.50 |
| Rubidium | (Ru) | 0.475 |
| Magnesium | (Mg) | Trace |
| Calcium | (Ca) | 9.26 |
| Aluminum | (Al) | |
| Anions | | |
| Fluoride | (F) | 0.46 |
| Chloride | (Cl) | 1.43 |
| Bromide | (Br) | 0.040 |
| Iodide | (I) | 0.0552 |
| Carbonate | ($CO_3$) | 29.59 |
| Sulfate | ($SO_4$) | 9.06 |
| Borate | ($BO_3$) | 0.152 |
| Phosphate | ($PO_4$) | Not Detected |
| Sulfide | (S) | Trace |

[a] This analysis is variable; however Radian has conducted various cement dust analyses and has found it to be about 40 percent potassium oxide equivalent. Complete analysis is not available. Also contains silicates and aluminates.

Source: EPA 600/2-79-111) Multimedia Assessment and Environmental Research Needs of the Cement Industry.

TABLE 5-9. HEAVY METALS CONTAINED IN KILN DUST SAMPLES, PARTS PER MILLION

| | |
|---|---|
| Zinc | 16,200 |
| Chromium | 110 |
| Lead | 5,620 |
| Manganese | 130 |
| Iron | 8,400 |
| Strontium | 150 |
| Cesium | 74 |
| Rubidium | 4,750 |

Source: EPA 600/2-79-111 Multimedia Assessment and Environmental Research Needs of Cement Industry.

of polymeric sulfur and their possibility of being retained in slag as stable compounds.

A study at Brookhaven National Laboratory[19] used commercial calcium silicate bearing Portland cement type III in the form of agglomerated cement sorbent (ACS) pellets for the in-situ desulfurization of fuel gases and for the improved gasification in a chemically active fluidized bed (CAFB) process. The reactions between Portland cement (represented by the chemical species tricalcium silicate) and $H_2S$ gas may be written as follows.

Sulfidation by the sorbent -

$$(CaO)_3SiO_2 + 3H_2S = (CaS)_3S_iO_2 + 3H_2O \qquad (5\text{-}33)$$

Regeneration of the sorbent -

$$\text{Partial oxidation:} \quad (CaS)_3SiO_2 + 6O_2 \rightarrow (CaSO_4)_3SiO_2 \qquad (5\text{-}34)$$

$$\text{Reduction:} \quad (CaSO_4)_3SiO_2 + 3CO \rightarrow (CaO)_3SiO_2 + 3CO_2 + 3SO_2 \qquad (5\text{-}35)$$

$$3(CaSO_4)_3SiO_2 + (CaS)_3SiO_2 = 4(CaO)_3SiO_2 + 12SO_2 \qquad (5\text{-}36)$$

or

$$\text{Reaction with } CO_2\text{:} \quad (CaS)_3SiO_2 + 9CO_2 = (CaO)_3SiO_2 + 3SO_2 + 9CO \qquad (5\text{-}37)$$

This process results in extraction of $H_2S$ and recovery of sulfur in the form of a concentrated stream. The concentrated $SO_2$ can be converted to sulfuric acid or may be reduced to elemental sulfur. The rate of sulfidation first increases with temperature following Arrhenius relations in the temperature range of 800 to 1000°C and then decreases with increase in temperature with the optimum being about 1000°C for sulfidation. The ACS pellets have a sulfur capture capacity of about 60 percent at 950°C and are 100 percent regenerable. Unfortunately the rate of sulfidation is markedly affected by the $CO_2$ content. From the thermogravimetric analysis (TGA) measurements of the sulfidation rates of the ACS pellets it was noted that two-hour sulfidation capacity of the pellets decreases from 51.7 percent to 32 percent when $CO_2$ content changes from 0 percent to 4 percent. Between 4 to 8 percent the capacity remains constant at 32 percent. Since the typically expected carbon dioxide concentration in the entrained-bed gasifiers may vary from 2 to 17 percent, the effectiveness of adding calcium silicate to the gasifier to scavenge the $SO_x$ precursors appears limited. In addition, no information is available on the $SO_2$ and calcium silicate reactions from this study which concentrated on the product gas with 0.5 percent $H_2S$ for desulfurization.

Morgantown Energy Research Center (MERC), in one of its programs, is exploring the possibility of hot gas contaminant control in the gasification process or the gasifier product stream. Hot gas cleanup of $H_2S$ in raw gas streams by chemisorption on supported metal oxides is at various stages of development. The report on Chemistry of Hot Gas Cleanup in Coal Gasification and Combustion[20] is a preliminary review of the chemistry of sulfur, nitrogen, alkali, halogen, and aluminosilicate compounds which occur as vapors or are associated with particulates in gasification and combustion atmospheres. The primary emphasis of this report pertains to the equilibrium thermodynamic information regarding the formation, phases, chemical states, reactions and deposition of these substances. Limited kinetic information is considered. Although the information and technology developed for hot gas cleanup of $H_2S$ in raw streams by chemisorption on supported metal oxides is not directly applicable to the in-process control of sulfur and nitrogen derived pollutants, some of the information may be useful for rational extrapolation.

The selection of metal oxides for scavenging of $H_2S$ was considered on the basis of their ability to remove $H_2S$ to comply with the 1977 EPA NSPS. Figure 5-5 presents the sulfur removal efficiencies attainable with metals in coal gas. An extrapolation of the shift in the exit gas concentrations of $H_2S$ with operating temperatures indicates that ZnO and $V_2O_3$ are the only

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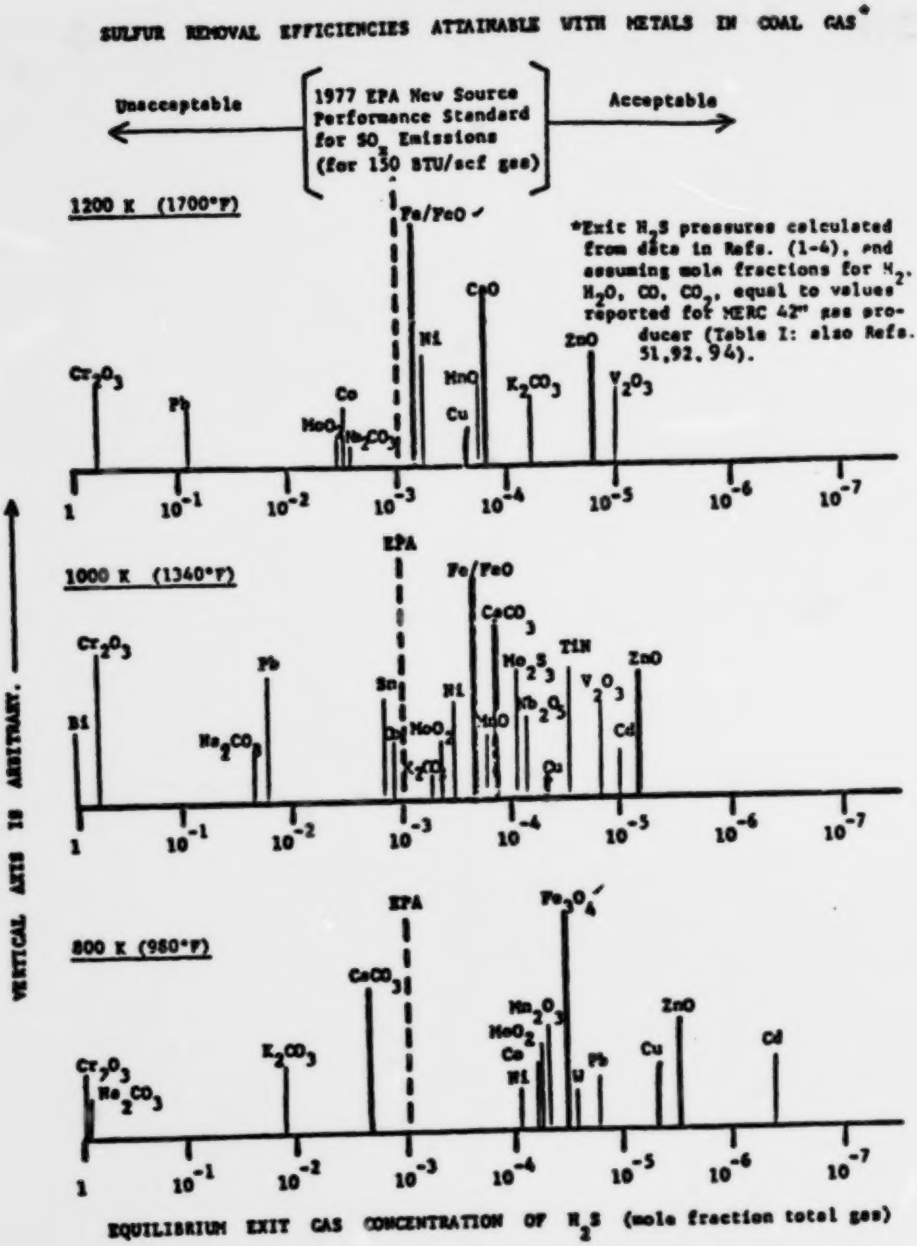

Figure 5-5. Sulfur removal efficiencies attainable with metals in coal gas.

Source: Morgantown Energy Research Center, MERC/SP-78/2, Chemistry of Hot Gas Cleanup in Coal Gasification and Combustion, 1978.

recyclable sorbents studied which are applicable at temperatures of 1,400 K to 1,600 K when one considers the fusion, vaporization problems and other attrition problems due to the side reactions occurring during sorbent regeneration. Figure 5-6 presents sulfidation kinetic data for the selected metal oxides.

Zinc oxide is the predominant form of zinc in $H_2S$ absorption because neither $H_2$ nor CO can reduce ZnO to zinc metal. Kinetically ZnO absorbs $H_2S$ more slowly than either $Fe_2O_3$, MnO, or CaO. Although the zinc sulfide melting point in the CRC Handbook of Chemistry and Physics[21] has been quoted as 1850°C at 150 atmospheres, it is known to sublime at 1185°C making it unsuitable for removal with the slag. Alternatively vanadium oxide, or $V_2O_3$, reacts with $H_2S$ in the product gas to generate vanadium sulfide

$$V_2O_3 + 3H_2S \longrightarrow V_2S_3 + 3H_2O \qquad (5\text{-}38)$$

Other sulfides of vanadium are not stable under hot product gas conditions. Sulfidation of vanadium proceeds much more slowly as compared to other metal oxides (Figure 5-6), hence its usefulness as a scavenger in the entrained-bed gasifier is doubtful.

In-situ sulfur fixation during the combustion of coal has been studied by Michael Smith.[22] The study is centered around preheating coal with sorbent powders and then analyzing the combustion gases. The high temperature combustion zone in a Burnell Model BT-1-9 furnace was operated at temperatures as high as 1425°C. The combustion conditions, however, did not parallel the entrained-bed slagging gasifier conditions. Hydrometallization reactions, in which the metal heteroatoms are removed concurrently with sulfur and the scavenging reactions take place in the hydrogen atmosphere, are useful in studying the catalytic action of metals. Vanadium hydrometallization reactions are promising but the process does not seem to appear suited to the entrained-bed gasifier wherein the sulfides need to be collected in the slag and not the product gas.

Table 5-10 presents a summary of various $H_2S$ removal processes used at present.[23] Most of these sorbents are effective only under mild conditions.

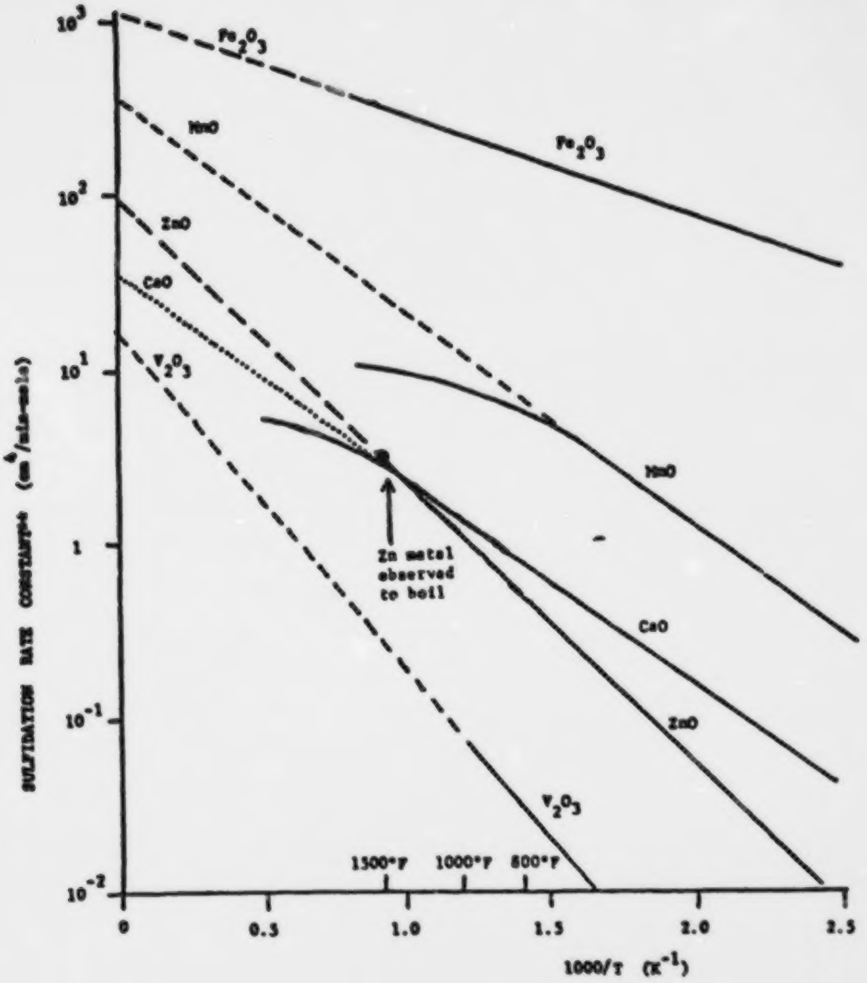

Figure 5-6. Kinetics of $H_2S$ absorption by selected metal oxides. Solid curves represent actual experimental data for sulfidation. Broken curves represent extrapolations of Arrhenius plots for reaction rate-controlled sulfidation.

Source: Morgantown Energy Research Center, MERC/SP-78/2, Chemistry of Hot Gas Cleanup in Coal Gasification and Combustion, February 1978.

## TABLE 5-10. SUMMARY OF TYPICAL $H_2S$ REMOVAL PROCESSES

| Process | Reactions | Products | Temp ($^oC$) | Pressure (atm) | Comments |
|---|---|---|---|---|---|
| **Alkaline Salts** | | | | | |
| Benfield | $K_2CO_3 + H_2S$  $KHS + KHCO_3$ | $H_2S$ | 65-110 | 6-60 | 1. Removal of $CO_2$, HCN, $NH_3$, COS, $CS_2$<br>2. Low solution Degradation<br>3. Low utility requirement |
| Catacarb | $K_2CO_3 + H_2S$  $KHS + KHCO_3$ | $H_2S$ | 65-110 | 6-60 | 1. Removal of $CO_2$, HCN, $NH_3$, COS, $CS_2$<br>2. Low solution Degradation<br>3. Low utility requirement |
| **Alkanol Amines** | | | | | |
| MEA | $HOC_2H_4NH_2 + H_2S$  $HOC_2H_4NH_3\ HS$ | $H_2S$ | 25-50 | High | 1. Removal of $CO_2$<br>2. Degradation by COS, $CS_2$, $O_2$ HCN<br>3. Low corrosion |
| Trencor | $(HOC_2H_4)_2NCH_3 + H_2S$  $(HOC_2H_4)_2NHCH_3\ HS$ | $H_2S$ | 50-110 | 1-50 | 1. Removal of $CO_2$<br>2. Degradation by HCN |
| Econamine | $HOC_2H_4OC_2H_4NH_2 + H_2S$  $HOC_2H_4OC_2H_4NH_3\ HS$ | $H_2S$ | 20-30 | High | 1. Removal of $CO_2$<br>2. Low solution Degradation |
| **Solvents** | | | | | |
| Selexol | (Dimethylether of polyethylene glycol) | $H_2S$ | 0-30 | High | 1. Removal of $CO_2$, HCN, $NH_3$, COS, $CS_2$<br>2. High solvent loading capacity<br>3. Low corrosion |
| Purisol | (N-methyl 2-pyrrolidone) | $H_2S$ | 20-30 | High | 1. Removal of $CO_2$, HCN, $NH_3$, COS, $CS_2$<br>2. High solvent loading capacity<br>3. Low corrosion |
| Rectisol | (Methanol) | $H_2S$ | -70--10 | High | 1. Removal of $CO_2$, HCN, $NH_3$, COS, $CS_2$<br>2. High solvent loading capacity<br>3. Low corrosion |
| **Liquid Oxidation** | | | | | |
| Stretford | $H_2S$  $HS^- + H^+$<br>$2V^{5+} + HS^-$  $2V^{4+} + H^+ + S$<br>$2V^{4+} + ADA + 2H^+$  $2V^{5+} + ADA(R)$<br>$ADA(R) + 1/2O_2$  $ADA + H_2O)$ | S | 10-30 | Lo/Hi | 1. Low solvent loading capacity<br>2. Degradation by HCN<br>3. High purity sulfur |
| Cataban | $2Fe^{3+} + H_2S$  $2Fe^{2+} + S + 2H^+$<br>$2Fe^{2+} + 1/2O_2$  $2Fe^{3+} + O^{2-}$ | S | - | Lo/Hi | 1. Low solvent loading capacity<br>2. Degradation by HCN<br>3. High purity sulfur |
| Takahax | $NQ + NaHS + NaHCO_3$  $HNQ + S + Na_2CO_3$ | S | - | Lo/Hi | 1. Low solvent loading capacity<br>2. Degradation by HCN<br>3. High purity sulfur |
| $HNQ + 1/2O_2$ | $NQ + H_2O$<br>$HNQ + 1/2O_2$  $NQ + H_2O$ | | | | |
| G-V | $KH_2AsO_3 + 3H_2S$  $KH_2AsS_3 + 3H_2O$<br>$HH_2AsS_3 + 3KH_2AsO_4$  $4KH_2AsO_3 + 3S$ | S | 30-150 | Lo/Hi | Toxic arsenic compounds |
| **Liquid Conversion** | | | | | |
| IFP | $SO_2 + 2H_2S$  $2H_2O + 3S$ | S | 30-150 | Low | Claus tail gas treatment |
| Townsend | $SO_2 + 2H_2S$  $2H_2O + 3S$ | S | 30-110 | High | Natural gas treatment |
| $CuSO_4$ | $Cu^{2+} + H_2S$  $CuS + 2H^+$ | $H_2SO_4/S$ | 180 | 10 | $H_2S$ removal from geothermal steam |
| **Solid Sorbents** | | | | | |
| Dry Box | $Fe_2O_3 + 6H_2S$  $2Fe_2S_3 + 6H_2O$ | S | 20-30 | 8-20 | 1. Low capacity<br>2. Incomplete regeneration |
| Frodingham | $Fe_2O_3 + 3/2H_2S$  $FeS\ FeS_2 + 3H_2O$ | $SO_2$ | 350-400 | 8-20 | 1. Low capacity<br>2. Incomplete regeneration |
| MERC | $Fe_2O_3 + 3/2H_2S$  $FeS\ FeS_2 + 3H_2O$ | $SO_2/S$ | 500-800 | 20 | |
| Dolomite | $CaCO_3\ MgO + H_2S$  $CaS\ MgO + H_2O + CO_2$ | $H_2S$ | 800-900 | 15 | Difficult regeneration |

For example, the MERC iron oxide process, dry box process, and Frodingham process are limited by mild temperature conditions and low capacity for sulfur capture. Iron oxides supported on pellets of fly ash or other inert material have been examined as $H_2S$ sorbent material. Thermodynamically, iron oxides should be effective. Since the oxides as well as the free metal can react with $H_2S$, it is important to consider which forms will exist in the gas stream. Iron oxides have been used and tested as hot $H_2S$ sorbents for coke oven gases for many years. It is known that more than one sulfide phase can exist for iron. Iron pyrite, $FeS_2$, is common at ambient temperature. However, at higher temperatures, $FeS_2$ is increasingly unstable making its formation difficult.

$$FeS + H_2S \longrightarrow FeS_2 + H_2 \qquad (5\text{-}39)$$

$$FeS_2 \longrightarrow FeS + S_2 \qquad (5\text{-}40)$$

At a sorbent temperature of 725°C, 1 to 10 percent elemental sulfur would have to be present in the product gas for pyrites to exist. Data beyond this temperature range are not availble. Apparently, these are limiting temperatures for $H_2S$ capture.

Thermodynamically and kinetically, one might expect manganese to behave similarly to magnesium or calcium. However, with respect to its oxides it behaves more like iron.

$$MnO + H_2S \longrightarrow MnS + H_2O \qquad (5\text{-}41)$$

In the product gas atmosphere, MnO is an active reagent with $H_2S$ and manganese-based sorbents are thermodynamically effective. For MnO particles with surface areas of 0.32 $m^2/gm$, the sulfidation kinetic rates are diffusion limited at temperatures above 475°C. Sulfidation by MnO occurs at rates on the order of 5 to 10 times as fast as those for CaO, but the rates are slower than for $Fe_2O_3$ sulfidation. Comparitive rates of sulfidation of CaO, $V_2O_3$, $Fe_2O_3$, and MnO are given in Figure 5-6. In the MERC program, MnO was not advocated as a sorbent due to undesirable side reactions and difficulties in regeneration. In a single pass entrained-bed gasifier, however, MnO may prove to be an attractive in-process sorbent depending on the stability of manganese sulfide.

Westmoreland, et al.,[24] conducted a systematic thermodynamic screening study of candidate sorbents for high-temperature desulfurization of gasifier product gases using the method of free energy minimization. The temperature range of interest was 400 to 1,200°C. The first step was to eliminate all oxides subject to reduction to low-melting point metals since these would be unstable at gasifier conditions. The criterion of acceptability was set at 95 percent gas desulfurization at equilibrium.

Oxides of 28 elements were considered in the analysis. Of these, only Mn, Zn, Ca, Ba, and Sr were projected to be acceptable above 1,000°C; above 1,200°C, only Ca, Ba, and Sr met the acceptability criteria. Barium sulfide melts above 1,200°C but this should not be a limitation in a slagging entrained-bed gasifier such as the Texaco unit. Sulfidation of strontium does not begin until 800°C, reaches the 95 percent level at 900°C, and exhibits maximum desulfurization near 1,100°C. The desulfurization potential of MnO drops off rapidly above about 1,100°C which limits its use in higher temperature regions of the gasifier.

Thermodynamic analyses do not address the physical phenomena, such as sintering and desurfacing, which may occur to solid sorbents at high temperatures. However, the analyses do indicate that barium and strontium (and perhaps manganese) should at least be considered and investigated as in-process sorbents for entrained-bed gasifiers along with lime and limestone.

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# 6.0 DEVELOPMENT OF A THEORETICAL MODEL

## 6.1 INTRODUCTION

In this study an investigation was made into the feasibility of developing a theoretical model for an entrained-bed slagging gasifier. The literature surveyed revealed that several existing models[1-8] had been proposed. It was then determined whether sufficient data and information were available to adapt an existing entrained-bed gasifier model to apply to the control of nitrogen and sulfur species in the gasifier.

The utility of a theoretical model is to be able to calculate what the exit conditions are for the entire range of operating conditions of the gasifier, and to be able to determine operating conditions which optimize desired parameters such as:

- maximize gas heating value,
- maximize char gasification,
- maximize CO-to-$H_2$ ratio,
- miminize $NO_x$ composition, and
- minimize $SO_x$ composition.

Operating conditions and parameters that the model should be able to incorporate are:

- coal feed rate,
- oxygen feed rate,
- $H_2O$/steam feed rate,
- CaO feed rate,
- feed stream (coal, $O_2$, $H_2O$, CaO) preheat,
- pressure,
- coal ultimate analysis,
- staged $O_2$ injection,
- staged $H_2O$ injection, and
- staged CaO injection.

A number of models have been developed for entrained-bed gasifiers.[1-8] In the latest model, Govind[1] has used the Texaco entrained-bed gasifier as a basis for the model, and has reviewed the bases for earlier models. Govind has used the results of 27 runs in the Texaco pilot plant gasifier to compare his model with experimental data[9,10]. A key feature of the Govind model, which makes it an attractive one with which to model the sulfur and nitrogen profiles in the Texaco gasifier, is that it used the unreacted-core shrinking model proposed by Wen.[11] Such a model postulates that since the reaction system is dilute, particle-particle interaction is neglected; therefore, the ash layer formed can be assumed to remain on the fuel particle during the reaction. The same model should apply when CaO is introduced with the coal, and when the solid-gas reactions involve CaO and $H_2S$ and/or CaO and HCN. In the case of CaO particles, instead of ash accumulation on the surface, the reaction products CaS or $CaCN_2$ would accumulate on the surface. The CaO would partially sinter, as indicated in Section 3, but as a first approximation the particle size could be assumed to remain relatively constant with little particle aggregation or agglomeration in the reactor. Govind's model appears to be the best model to date to be used to apply the theoretical concepts proposed in this study to calculate the nitrogen and sulfur species compositions at various points in the reactor.

## 6.2 GASIFIER MODEL

The discussion that follows uses Govind's approach to derive the mathematical model for an entrained-bed gasifier. The gasifier can be divided into at least two main sections: (1) the pyrolysis and volatile combustion section, and (2) the combustion and gasification section. The pyrolysis reaction releases the moisture and volatile matter in the raw fuel, is among the first to occur, and is the fastest among the reactions. Volatile combustion reactions include:

$$CO + \frac{1}{2} O_2 \rightleftharpoons CO_2 \tag{6-1}$$

$$H_2 + O_2 \rightleftharpoons H_2O \tag{6-2}$$

$$CH_4 + \frac{3}{4} O_2 \rightleftharpoons CO + 2H_2O \tag{6-3}$$

$$\text{Hydrocarbons} + zO \rightleftharpoons xCO_2 + y\ H_2O \tag{6-4}$$

The hydrocarbons in Reaction 6-4 were assumed to be $C_6H_6$. Other reactions of the gaseous volatile components are possible such as cracking reactions and further combustion of hydrocarbons to CO, instead of $CO_2$ as in Reaction 6-4. Govind used the results of Loison and Chauvin[15] to estimate the gaseous composition in the pyrolysis zone as a function of the fraction of the volatile material released. In Govind's treatment all the sulfur volatilized was assumed to become $H_2S$, while the fuel-bound nitrogen was assumed to gasify as nitrogen molecules ($N_2$). To improve Govind's model for the sulfur and nitrogen species, about 2.5 percent of the sulfur[17] should be assumed to volatilize as $SO_2$ with the remainder as $H_2S$. All of the fuel bound nitrogen can be assumed to volatilize as HCN.

### 6.2.1 Coal Pyrolysis and Volatile Combustion Zone

The equations Govind uses for the rate of coal pyrolysis are applicable without any modification. Once the pyrolysis begins, all of the heterogeneous gas-solid reactions are at a temperature between 1200°C and 2400°C, which means that diffusion through the gas film and the ash layer (or $CaS/CaCN_2$ layer) would be the controlling factor in the gasification. In the pyrolysis and volatile combustion zone, reaction rate expressions would need to be developed for the reactions of HCN, $SO_2$, and $H_2S$ with CaO.

$$CaO + H_2S \rightleftharpoons CaS + H_2O \tag{6-4}$$

$$CaO + SO_2 + \frac{1}{2} O_2 \rightleftharpoons CaSO_4 \qquad (6\text{-}6)$$

$$CaO + 2\ HCN \rightleftharpoons CaCN_2 + CO + H_2 \qquad (6\text{-}7)$$

The overall rate expression for a heterogeneous reaction can be expressed as:

$$\text{Rate} = \frac{1}{\frac{1}{K_{diff}} + \frac{1}{K_{ash}}\ \frac{y-1}{y} + \frac{1}{y^2 K_s}} (P_\ell - P_\ell^*) \qquad (6\text{-}8)$$

where $K_{diff}$ = gas diffusion constant, which is directly proportional to the gas diffusivity, and inversely proportional to the total pressure and particle diameter.

$K_{ash}$ = ash film diffusion constant which is proportional to $K_{diff}$ and the ash or slag fraction void.

$y$ = $r_c/R_p$, where $r_c$ is the radius of the unreacted-core-shrinking particle and $R_p$ is the outside radius of an unreacted-core-shrinking particle.

$K_s$ = the surface reaction rate constant.

$P_\ell - P_\ell^*$ = the effective partial pressure of gas, taking into account the reverse reaction effect.

A number of studies[16-19] have been devoted to the $CaO\text{-}H_2S$ and $CaO\text{-}SO_2$ reactions and their kinetics. Values for $K_s$ are available from these studies for Reactions 6-5 and 6-6. Attar[20] considers Reaction 6-6 to be much less important than Reaction 6-5 at temperatures above 1000°C, which would be found in entrained-bed coal gasification units.

The third reaction, Reaction 6-7, has been studied[21-25], but the references to the reaction are primarily in the Russian literature. The only kinetic study reported to date is in Reference 25.

### 6.2.2 Combustion and Gasification Zone

In the combustion and gasification section of the Texaco entrained-bed gasifier, several char-gas reactions are occurring, the CaO gas reactions continue, and gas-phase reactions occur. The gaseous combustion reactions given in Reactions 6-1 through 6-4 continue, but because the entire combustor operates in a fuel rich mode, these reactions are essentially at equilibrium. High temperatures (1,350 to 1,500°C) favor the reverse of Reaction 6-1, and low concentration of hydrocarbons by the time the combustion-gasification zone is reached, lessens the importance of Reactions 6-3 and 6-4.

6.2.2.1. Char-Gas Reactions. Govind[1] used kinetic reaction equations based on previous studies.[25,29]

Char-Oxygen Reaction

$$C_aH_bO_cN_dS_eA + \left( \frac{a}{\phi} - \frac{c}{2} + \frac{b}{2} - \frac{e}{2} \right) O_2 \longrightarrow 2\,(1-1/\phi)\,aCO + (2/\phi - 1)\,aCO_2$$

$$+ \left( \frac{b}{2} - e \right) H_2O + eH_2S + \frac{d}{2} N_2 + \text{ash} \qquad (6\text{-}9)$$

where: C, H, O, N, S, A are carbon, hydrogen, oxygen, nitrogen, sulfur, and ash, respectively,

a, b, c, d, e are stoichiometric coefficients for C, H, O, N, and S, respectively, and

$\phi$ is a shape factor.

Note that Govind has all the sulfur reacting to $H_2S$ and the fuel-bound nitrogen to $N_2$. In the proposed model, the nitrogen oxidized from the char would form HCN initially resulting in Reaction 6-10 replacing Reaction 6-9.

$$C_aH_bO_cN_dS_eA + \left( \frac{a}{\phi} - \frac{c}{2} + \frac{b}{2} - \frac{e}{2} - \frac{3d}{4} \right) O_2 \longrightarrow 2 \left(a - \frac{a}{\phi} - \frac{d}{4} \right) CO + \left( \frac{2a}{\phi} - a - \frac{d}{2} \right) CO_2 + \left( \frac{b}{2} - \frac{d}{2} - e \right) H_2O + eH_2S + dHCN + \text{ash} \tag{6-10}$$

Likewise the reactions given in Govind's paper[1], the Char-Steam Reaction,

$$C_aH_bO_cN_dS_eA + (a - c) H_2O \longrightarrow aCO + \left(a - e + \frac{b}{2} - e\right) H_2 + eH_2S + \frac{d}{2} N_2 + \text{ash}, \tag{6-11}$$

The Char Carbon-Dioxide Reaction,

$$C_aH_bO_cN_dS_eA + aCO_2 \longrightarrow 2aCO + \frac{c}{2} H_2O + \left( \frac{b}{2} - e - c \right) H_2 + eH_2S + \frac{d}{2} N_2 + \text{ash, and} \tag{6-12}$$

the Char-Hydrogen Reaction,

$$C_aH_bO_cN_dS_eA + \left( 2a + c + e - \frac{b}{2} \right) H_2 \longrightarrow aCH_4 + cH_2O + eH_2S + \frac{d}{2} N_2 + \text{ash}, \tag{6-13}$$

would have to be changed to have the fuel-bound nitrogen react to HCN, in a manner similar to that shown in Equation 6-10.

To the char-gas reactions in the combustion and gasification section must be added the heterogeneous solid-gas reaction,

$$CaO - H_2S, \; CaO - SO_2, \text{ and } CaO - HCN,$$

given above in Reactions 6-5, 6-6, and 6-7.

6.2.2.2 Gas-Phase Reactions. The gas-phase reactions given by Govind for the gasification section are the water-gas shift reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (6\text{-}14)$$

and the methane-steam reaction,

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2. \qquad (6\text{-}15)$$

To these gaseous reactions should be added those involving sulfur[20] compounds and nitrogen compounds.[29,30]

$$H_2S + H_2O \rightleftharpoons SO_2 + 2H_2 \qquad (6\text{-}16)$$

$$H_2S + CO_2 \rightleftharpoons COS + H_2O \qquad (6\text{-}17)$$

$$COS + H_2S \rightleftharpoons CS_2 + H_2O \qquad (6\text{-}18)$$

$$HCN + O \rightleftharpoons NCO + H \qquad (6\text{-}19)$$

$$NCO + H \rightleftharpoons NH + CO \qquad (6\text{-}20)$$

$$CO + OH \rightleftharpoons CO_2 + H \qquad (6\text{-}21)$$

$$NH + H \rightleftharpoons N + H_2 \qquad (6\text{-}22)$$

$$N + NO \rightleftharpoons N_2 + O \qquad (6\text{-}23)$$

$$N + OH \rightleftharpoons NO + H \qquad (6\text{-}24)$$

$$H + O_2 \rightleftharpoons OH + O \qquad (6\text{-}25)$$

$$HCN + OH \rightleftharpoons CN + H_2O \qquad (6\text{-}26)$$

$$HCN + O \rightleftharpoons NH + CO \qquad (6\text{-}27)$$

$$HCN + O \rightleftharpoons CN + OH \qquad (6\text{-}28)$$

$$CN + H_2 \rightleftharpoons HCN + H \qquad (6\text{-}29)$$

$$CN + O \rightleftharpoons CO + N \qquad (6\text{-}30)$$

$$CN + O_2 \rightleftharpoons NCO + O \qquad (6\text{-}31)$$

$$CN + OH \rightleftharpoons NCO + H \qquad (6\text{-}32)$$

$$N + O_2 \rightleftharpoons NO + O \qquad (6\text{-}33)$$

$$OH + H_2 \rightleftharpoons H_2O + H \qquad (6\text{-}34)$$

$$O + H_2 \rightleftharpoons OH + H \qquad (6\text{-}35)$$

$$H + O_2 + M \rightleftharpoons HO_2 + M \qquad (6\text{-}36)$$

$$H_2 + M \rightleftharpoons H + H + M \qquad (6\text{-}37)$$

$$NH_3 + O \rightleftharpoons NH_2 + OH \qquad (6\text{-}38)$$

$$NH_3 + OH \rightleftharpoons NH_2 + H_2O \qquad (6\text{-}39)$$

$$NH_3 + H \rightleftharpoons NH_2 + H_2 \tag{6-40}$$

$$NH_2 + NO_2 \rightleftharpoons NH_3 + O_2 \tag{6-41}$$

$$NH_2 + H + M \rightleftharpoons NH_3 + M \tag{6-42}$$

Thermodynamic and kinetic parameters for these reactions are available[30,31,32] in the temperature range found in the Texaco entrained-bed gasifier.

## 6.3 MODEL DEVELOPMENT

Govind[1] formulated a steady-stage one-dimensional model for the reactor system. A number of assumptions were made:

1. The solid-gas phases were assumed to be completely mixed. A stepwise approach was taken to integrate the kinetic, material balance, momentum balance, and energy balance equations. Each stepwise compartment in the integration was treated as a stirred tank reactor, i.e., the temperature and bulk stream composition were uniform throughout the compartment.

2. Radial dispersion was neglected.

3. Interactions among particles were neglected; the ash layer was assumed to remain on the char particle surface. Hence, the unreacted core-shrinking model was assumed.

4. Ideal gas equation of state was assumed to hold.

5. The temperature of the solid was uniform throughout the particle.

6. The ash was assumed to be inert as it remained with the particle. No catalytic effect of the ash was accounted for.

7. The frictional force between the phases and the wall was neglected.

8. No particle attrition was assumed.

9. Potential, and kinetic energies were considered negligible compared to thermal energies.

The only changes to the assumptions needed for a model with the in-process $NO_x$-$SO_x$ control proposed in this study would be that added assumptions would need to be made about the CaO particles in the reactor. CaO is known[33] to sinter and to lose reaction surface area at the temperatures to be found in the entrained bed gasifier. The voidage fraction of the CaO particles would therefore need to be reduced from any measured values at ambient temperature.

In Govind's solution procedure one centimeter stepwise increments were used in a reactor whose total length was 3.3 meters long. For each increment the following equations were written:

- solid-phase mass balance,
- gas-phase mass balance,
- solid-phase momentum balance,
- gas-phase momentum balance,
- solid-phase thermal balance, and
- gas-phase thermal balance.

in addition to the kinetic equations indicated above. In the Govind treatment the solid-phase mass balance accounted for the reaction of the char. In the proposed model, the solid-phase mass balance would add terms necessary to account for the reactions involving CO, HCN, and $H_2S$, in addition to the char reactions. Likewise, the gas-phase mass balance equations would account for the reactions of $H_2S$, and HCN in addition to the other homogeneous gas-phase reactions of the sulfur and nitrogen species.

The procedure used by Govind would be used to solve the model equations. The procedure is diagrammed in Figure 6-1. The calculation follows the following flow pattern. For each incremental compartment,

1. An average temperature and pressure are assumed,
2. A residence time is estimated from the flow rates of the reactants,
3. A conversion is calculated for each reaction from the kinetic equations and the residence time,
4. A pressure drop is calculated from the momentum balance equation,
5. A new average pressure is estimated,
6. A temperature change across the compartment is calculated from the energy balance equation,
7. A new average temperature is estimated,
8. Steps 1 through 7 are repeated until the temperature and pressure does not differ from the previous temperature and pressure a significant amount, and
9. Steps 1 through 8 are taken for the next incremental compartment, until the entire axial length of the reactor has been covered.

Sufficient kinetic and thermodynamic data are available to revise the Govind and Shah gasifier model to be able to predict the gasifier

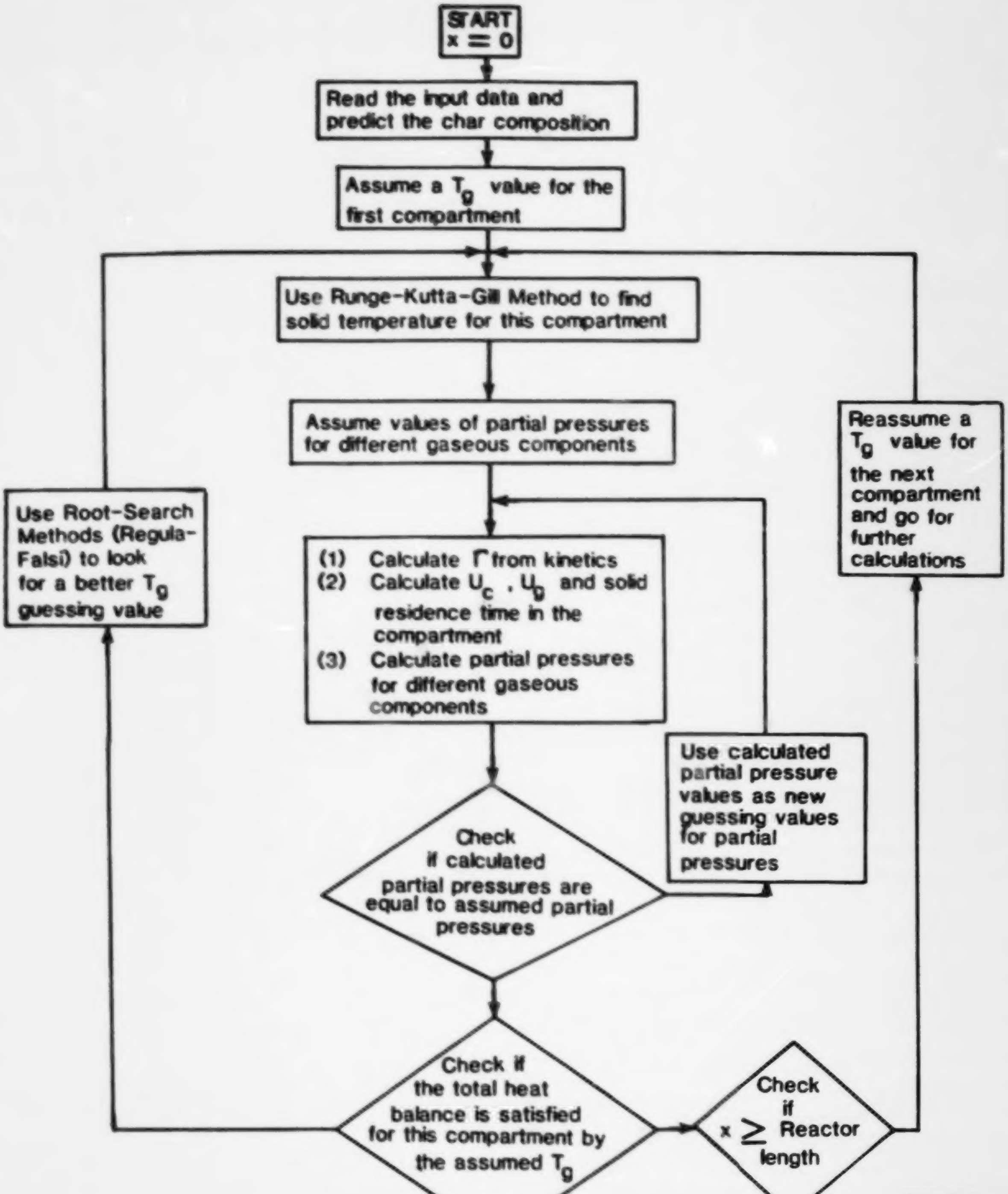
START
x = 0
Read the input data and predict the char composition
Assume a $T_g$ value for the first compartment
Use Runge-Kutta-Gill Method to find solid temperature for this compartment
Assume values of partial pressures for different gaseous components
(1) Calculate $\Gamma$ from kinetics
(2) Calculate $U_c$, $U_g$ and solid residence time in the compartment
(3) Calculate partial pressures for different gaseous components
Check if calculated partial pressures are equal to assumed partial pressures
Use calculated partial pressure values as new guessing values for partial pressures
Check if the total heat balance is satisfied for this compartment by the assumed $T_g$
Use Root-Search Methods (Regula-Falsi) to look for a better $T_g$ guessing value
Check if $x \geq$ Reactor length
Reassume a $T_g$ value for the next compartment and go for further calculations
STOP

Figure 6-1. Computer flow diagram for solving the model equations.

concentration profiles of $H_2S$, $SO_2$, COS, NO, $NH_3$, HCN and $N_2$. The assumption that would be most seriously in question relates to the effect of the gasifier conditions on the surface area of CaO available for reaction with $H_2S$ and HCN. As indicated above, the first assumption could be that the unreacted core-shrinking model applies to the CaO. Sintering of CaO in the reactor may require application of a fractional constant decreasing the area of CaO available for reaction as a second assumption. A third model may require that the available surface area for reaction decreases as a function of the amount of CaS + CaNCN reacted. The model could be derived to accommodate to these three assumptions to determine what effect these approximations may have on the final gaseous compositions leaving the gasifier.

Experimental data are ultimately required in order to check out the model calculations. If there are serious discrepancies between the model and the calculated results, then some of the assumptions made in the model development will need to be reviewed and revised until a satisfactory model can be built. At present there appears to be insufficient experimental data in the published sources relative to the nitrogen and sulfur gas species leaving an entrained-bed gasifier fed with pulverized coal, water, oxygen, and CaO to be able to tune a theoretical model completely. Sufficient data are, however, available to be able to determine if the $SO_x$ and $NO_x$ controls proposed in this study warrant further experimental or theoretical verification. Bench-scale data could provide the data needed to help validate the model.

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# 7.0 ASSESSMENT OF GASIFIER PRODUCT GASES AS GAS TURBINE FUELS

One of the objectives of this study is to determine the implications of using gasifier product gases as gas turbine fuels in terms of the effects on gas turbine performance, efficiency, and emissions. To accomplish this objective, it will be necessary to determine the level of emissions control required in the gasifier or in the gasifier cleanup train in order to meet existing emission limits and fuel specifications for gas turbines.

This section provides general information on gas turbine design and operation, as well as data and information on emissions from gas turbines, and emission control techniques available for gas turbines. The potential impacts associated with firing gasifier product gases in gas turbines are then examined and discussed.

## 7.1 GAS TURBINE EMISSIONS AND CONTROLS

### 7.1.1 Description of Gas Turbines[1]

A gas turbine, or combustion turbine, is basically a heat engine which transfers the heat of combustion to compressed hot air which, in turn, is expanded through a turbine to produce mechanical work through a rotary shaft. A basic flow diagram for a gas turbine is presented in Figure 7-1. As shown, the major components of a typical gas turbine are the compressor, the combustor, and the turbine. The compressor serves to increase the pressure (and the temperature) of the combustion air. Gas turbines typically operate at pressures ranging from 5 to 30 atmospheres. In the combustor section, which consists of four zones, a gaseous or liquid fuel is burned with the combustion air. In the inlet transition zone, the velocity of the fuel and air streams are reduced, resulting in a pressure drop across this zone. In the primary combustion zone, fuel is injected and fired at near stoichiometric ratios, resulting in peak temperatures ranging from 2800°F to 4500°F.[2] In the secondary combustion zone, additional air is added to ensure complete combustion and to reduce the temperature quickly to

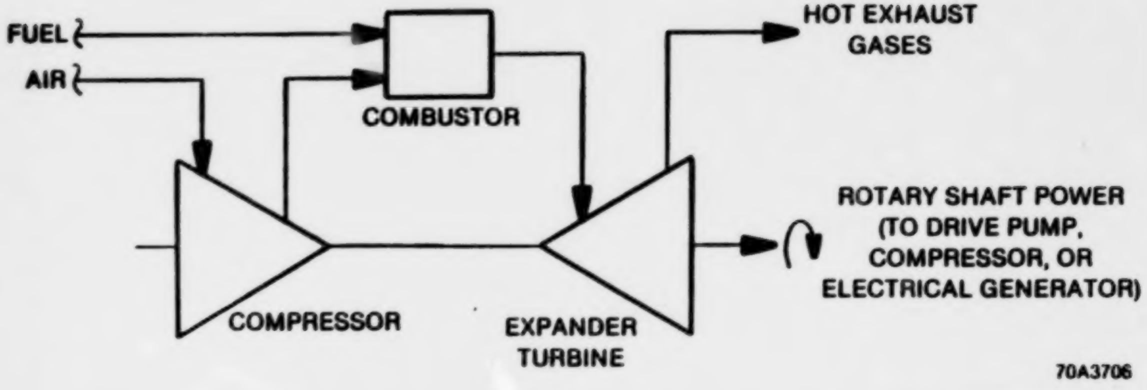
FUEL
AIR
COMBUSTOR
COMPRESSOR
EXPANDER TURBINE
HOT EXHAUST GASES
ROTARY SHAFT POWER (TO DRIVE PUMP, COMPRESSOR, OR ELECTRICAL GENERATOR)
70A3706

Figure 7-1. Basic gas turbine flow diagram.

a range more compatible with combustor and turbine materials. In the outlet transition zone, the hot gases are passed through an accelerator to increase their velocity before entering the turbine. The turbine firing temperature, or combustor exit temperature, is an important design parameter in gas turbines, with typical temperatures ranging from 1200°F to 2000°F. Finally, the hot gases are expanded across one or more turbine stages to provide shaft power to drive pumps, compressors, and/or electrical generators.

Typical efficiencies for gas turbines range from 21 to 38 percent, where efficiency is defined as the rated energy output of the turbine divided by the energy of the fuel input. Factors affecting gas turbine efficiency include, in general order of importance, pressure and firing temperature, design characteristics and efficiencies of the compressor and turbine sections, pressure drop across the combustor, and heat and mechanical losses.

The efficiency of a gas turbine also depends on its arrangement with respect to other processes. Gas turbines that produce no energy other than shaft power are called simple-cycle gas turbines, and are generally the least efficient type of system. In a regenerative-cycle gas turbine, the gas turbine exhaust is used to preheat the combustion air, resulting in improved overall efficiency. In a cogeneration/combined cycle system, the gas turbine exhaust is used as a direct heat source or to produce steam in a heat recovery steam generator; this steam is then used as process steam to drive a steam turbine or for other purposes.

### 7.1.2 Applicable Emission Limits and Fuel Specifications

Gas turbines produce nitrogen oxides ($NO_x$), sulfur oxides ($SO_x$), particulate matter (PM), carbon monoxide, hydrocarbons, and visible emissions.

$NO_x$ and $SO_2$ emissions from new, modified, or reconstructed gas turbines are regulated under 40 CFR 60 Subpart GG.[3] The $NO_x$ emission limitations for fuels with fuel-bound nitrogen contents less than 0.015 weight percent are:

- 75 ppmv $NO_x$ for electric utility stationary gas turbines with a heat input at peak load greater than 100 million Btu/hour based on the lower heating value of the fuel; and

- 150 ppmv $NO_x$ for stationary gas turbines with a heat input at peak load greater than 10 million Btu/hour but less than or equal to 100 million Btu/hour based on the lower heating value of the fuel.

These limitations are expressed on a dry basis at 15 percent excess oxygen in the exhaust gas and apply to units with a manufacturer's rated heat rate at peak load of 14.4 kilojoule/watt-hr (13,650 Btu/kw-hr). For lower heat rates, the limit would be increased proportionally. An emission allowance is granted for fuels with nitrogen contents above 0.015 weight percent. These nitrogen content specifications refer to the fuel gas combusted in the turbine, not the coal fed to the gasifier in a combined gasifier-turbine system. Corrections to the $NO_x$ limits are also specified in Subpart GG for the effects of combustor inlet pressure, ambient temperature, and humidity, but these corrections should be minimal for a typical facility. Based on the estimated concentrations of $NH_3$ and HCN in raw medium- and low-Btu gasifier product gases (as shown in Table 2-5), this $NO_x$ emission allowance is calculated to be about 40 ppmv and 20 ppmv, respectively.

The requirements of 40 CFR 60 Subpart GG also restrict the sulfur content of the fuel gas and the $SO_2$ emissions in the gas turbine exhaust. The sulfur content in the gas turbine fuel cannot exceed 0.8 weight percent, and the $SO_2$ concentration of the gas turbine exhaust cannot exceed 150 ppm (dry basis, 15 percent $O_2$). The $SO_2$ limitation of 150 ppm corresponds to a product gas sulfur content of about 0.10 mole percent for both medium-Btu gas and low-Btu gas.

In addition to the new source performance standards (NSPS) regulating the emissions of $NO_x$ and $SO_2$, there are manufacturers' design specifications which limit the concentration of $SO_2$ and particulate matter precursors in gas turbine fuels. The $H_2S$ content of gas turbine fuels is limited to 0.18 mole percent, based on equipment considerations.[4] The $H_2S$ restriction arises out of corrosion considerations since $H_2S$ will form oxides and sulfates in the combustor. These compounds subsequently undergo corrosion reactions with the turbine metal. Although not specified, this sulfur limitation should also apply to other trace sulfur compounds in the gasifier product gas such as $CS_2$ and COS which will also form oxides and sulfates in the combustor. Thus, a conservative sulfur limitation for gasifier product gas would be 0.18 mole percent based on total sulfur species.

Particulate matter in gas turbine fuels is undesirable in that it can cause erosion of turbine blades by impaction. Fuel specifications for natural gas limit total particulate matter to 30 ppmw, with no particles larger than 10 μm; this corresponds to an exhaust gas concentration of 0.45 ppmw total particulates.[5] For fuels other than natural gas, the allowable PM loading would be that concentration corresponding to a concentration of 0.45 ppmw in the exhaust gas. Since gasifier product gases have a lower air-to-fuel ratio in the turbine, the allowable PM loading for these gases is lower than that for natural gas. In addition to limitations on total particulate matter, there are also limitations on concentrations of individual alkali trace metals, which can corrode the turbine metal. Limitations of these individual trace metals in the turbine exhaust gas are as follows:[5,20]

- 0.024 ppmw of Na plus K.
- 0.01 ppmw of V,
- 0.02 ppmw of Pb, and
- 0.01 ppmw of Ca.

In addition to the individual limits, the imposed limit on total trace metal concentration in the exhaust gas is 0.024 ppmw. As stated above, the fuel gas specifications corresponding to these outlet concentrations are dependent upon the air-to-fuel ratio in the turbine. Table 7-1 presents approximate specifications for total particulate matter and for trace metals for various fuel types.

## TABLE 7-1. FUEL SPECIFICATIONS FOR PARTICULATE MATTER AND TRACE METALS[a]

| Fuel Type | Lower Heating Value (Btu/scf) | Approximate Air-to-Fuel Mass Ratio[b] | Allowable Concentration in the Fuel, ppmw[c] | | | | |
|---|---|---|---|---|---|---|---|
| | | | Total PM | Na + K | V | Pb | Ca |
| Natural Gas | 1,025 | 61.0 | 30 | 1.5 | 0.6 | 1.2 | 0.6 |
| Medium-Btu Gas | 320 | 13.5 | 6.5 | 0.4 | 0.15 | 0.3 | 0.15 |
| Low-Btu Gas | 110 | 4.2 | 2.3 | 0.12 | 0.05 | 0.10 | 0.05 |

[a] Reference 5.

[b] Based on total air feed to gas turbine.

[c] Based on the following limitations on contaminant concentration in the combustion products:

Total PM: 0.45 ppmw
Na + K: 0.024 ppmw
V: 0.01 ppmw
Pb: 0.02 ppmw
Ca: 0.01 ppmw

Also assumes that the concentration of contaminants in the combustion air is negligible.

### 7.1.3 Factors Affecting Emissions From Gas Turbines

As stated above, gas turbines produce $NO_x$, $SO_x$, particulate matter, carbon monoxide, hydrocarbons, and visible emissions. The quantity of each of these pollutants emitted is dependent on the type of fuel fired, design characteristics and efficiency, and operating load. Each of these pollutants and the factors affecting the emissions of these pollutants from gas turbines are discussed below.

7.1.3.1 Nitrogen Oxides ($NO_x$). Nitrogen oxides, including NO, $NO_2$, and the less important species of $N_2O$, $N_2O_5$, etc., are formed by two different mechanisms to produce "thermal $NO_x$" and "fuel $NO_x$." Thermal $NO_x$ is produced by the high temperature reaction of molecular nitrogen in the combustion air (or molecular nitrogen, i.e., "free" nitrogen, in the fuel) with oxygen in the combustion air. Fuel $NO_x$ is produced by the reaction of fixed nitrogen in the fuel (e.g., $NH_3$ and HCN) with oxygen in the combustion air.

The Zeldovich mechanism is commonly used to describe the formation of thermal $NO_x$. The Zeldovich equation for the formation rate of thermal $NO_x$ is expressed as follows:[6]

$$\frac{dX_{NO}}{dt} = k \left[P^{0.5}\right] \left[X_{O_2}^{\;0.5}\right] \left[X_{N_2}\right] \left[\frac{1}{T_f}\right] \exp\left[\frac{-122{,}000}{T_f}\right] \left[1 - \frac{X_{NO}}{(X_{NOe})^2}\right]$$

where:

$k$ = constant of formation

$P$ = combustion pressure (absolute)

$T_f$ = flame temperature

$X$ = the volumetric fraction of the substance (e.g., $O_2$, $N_2$, NO)

$X_{NOe}$ = nitric oxide equilibrium concentration, volume fraction

This equilibrium relationship indicates that thermal $NO_x$ formation increases exponentially with increases in flame temperature, increases directly with $N_2$ concentration, and increases directly with the square root of the $O_2$ concentration and the square root of the combustion pressure. These effects are discussed quantitatively below.

The Zeldovich equation implies that flame temperature has the greatest impact on $NO_x$ emissions. The combustion flame temperature is a function of the heating value of the fuel, the combustion efficiency, and the combustor inlet conditions. For a given set of firing conditions, the flame temperature for medium-Btu product gases ($O_2$-blown) is higher than that of natural gas, while the flame temperature for low-Btu product gases (air-blown) is significantly lower than that of natural gas.[7] Medium-Btu gases have relatively high flame temperatures due to their low air-to-fuel requirements, while low-Btu gases have low flame temperatures due to the high concentration of $N_2$ in the fuel ($N_2$ in the fuel or air serves as a heat sink and therefore reduces the flame temperatures). Thus, the $NO_x$ emissions associated with the firing of medium-Btu gases should be higher than those for natural gas, while the $NO_x$ emissions associated with the firing of low-Btu gases should be significantly lower than those for natural gas.

$NO_x$ emissions are generally reported in terms of the turbine firing temperature (combustor exit temperature). Figure 7-2 shows the effects of firing temperature on $NO_x$ emissions for various fuels fired in a conventional gas turbine combustor. Figure 7-2 shows that $NO_x$ emissions increase dramatically with increases in firing temperature for each fuel type. Figure 7-2 also shows that the differences in $NO_x$ emissions between fuel types is magnified as firing temperature increases. As predicted by the Zeldovich equation, $NO_x$ emissions for medium-Btu gases are higher than those for natural gas, while $NO_x$ emissions for low-Btu gases are lower than those for natural gas. It should be noted that, although reducing the firing temperature can result in reduced $NO_x$ emissions, it also results in reduced turbine efficiencies.

The Zeldovich equation also predicts increased thermal $NO_x$ emissions with increased combustor pressure. Figure 7-3 presents a manufacturer's

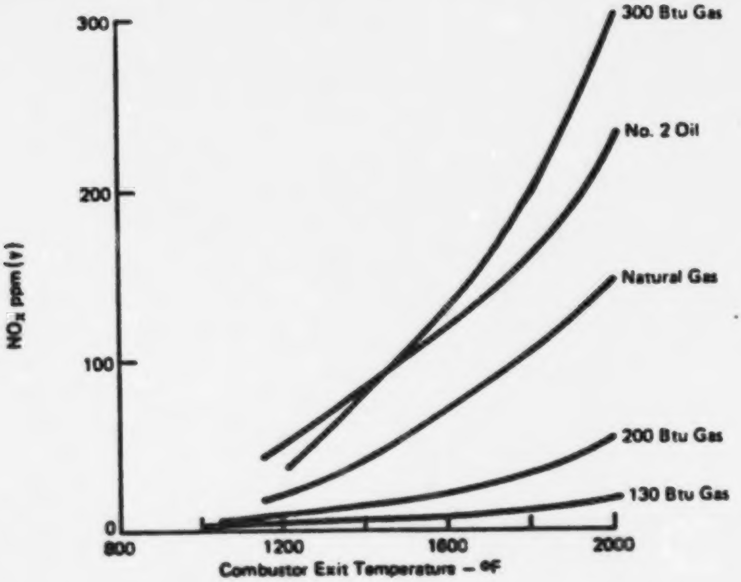

Figure 7-2. $NO_x$ emissions for various fuels fired in a conventional gas turbine combustor.[8]

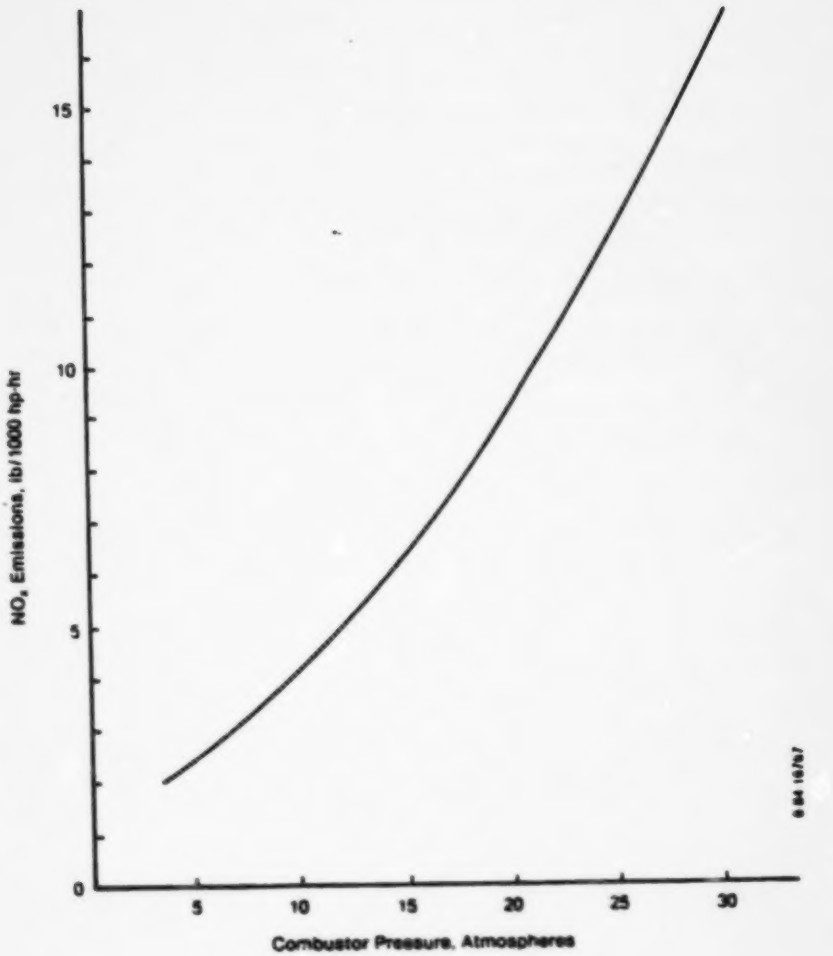

Figure 7-3. Gas turbine NO$_x$ emissions versus combustor pressure for natural gas.[9]

curve of $NO_x$ versus combustor pressure for natural gas. Again, similar results are expected for gas turbines firing gasifier product gases. Figure 7-4 shows the combined effects of firing temperature and pressure for medium-Btu gases fired in a test combustor. Although decreasing the combustor pressure can reduce $NO_x$ emissions it also results in a decreased turbine efficiency.

The exact mechanism for the formation of fuel $NO_x$ is not well known, but is known to be proportional to the fuel nitrogen content. Natural gas and distillate oil, the traditional gas turbine fuels, contain negligible amounts of fuel nitrogen and therefore fuel $NO_x$ is generally unimportant when firing these fuels. However, gasifier product gases may contain various levels of $NH_3$ and HCN, depending on the gas cleaning techniques employed prior to combustion in a gas turbine. Figure 7-5 shows that the efficiency of conversion of fuel nitrogen to $NO_x$ for liquid fuels is about 100 percent at concentrations of 0.03 weight percent nitrogen or less, decreasing to about 50 percent conversion at a fuel nitrogen content of 0.2 weight percent.

Currently, the most widely used control method which is effective in reducing $NO_x$ emissions from gas turbines firing gasifier product gases is injection of water or steam into the combustor. The injection of water or steam into the combustor serves to lower the peak flame temperature and therefore reduces thermal $NO_x$ emissions. Typical water injection rates range from 0.3 to 1.0 lb of water per pound of fuel; typical steam injection rates are 0.5 to 2.0 lb steam per lb of fuel, or about twice the injection rate of water.[12] The steam injection rate must be higher than the water injection rate to achieve a given $NO_x$ emissions reduction since the water has a much greater heat absorbing capacity. Figure 7-6 shows the effects of water and steam injection rate on $NO_x$ emissions for a gas turbine firing natural gas. Figure 7-6 shows that the emissions reductions achieved increase with increasing water or steam injection rate, but that the incremental emissions reduction achieved decreases as injection rate increases.

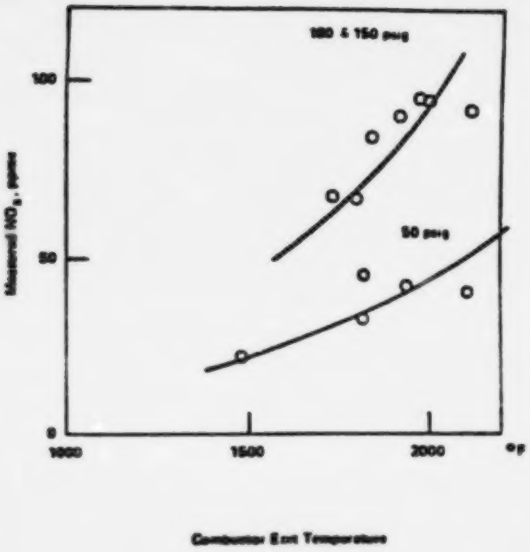

Figure 7-4. Medium-Btu gas results 5/18/81 test $NO_x$ vs. $T_{avg}$.[10]

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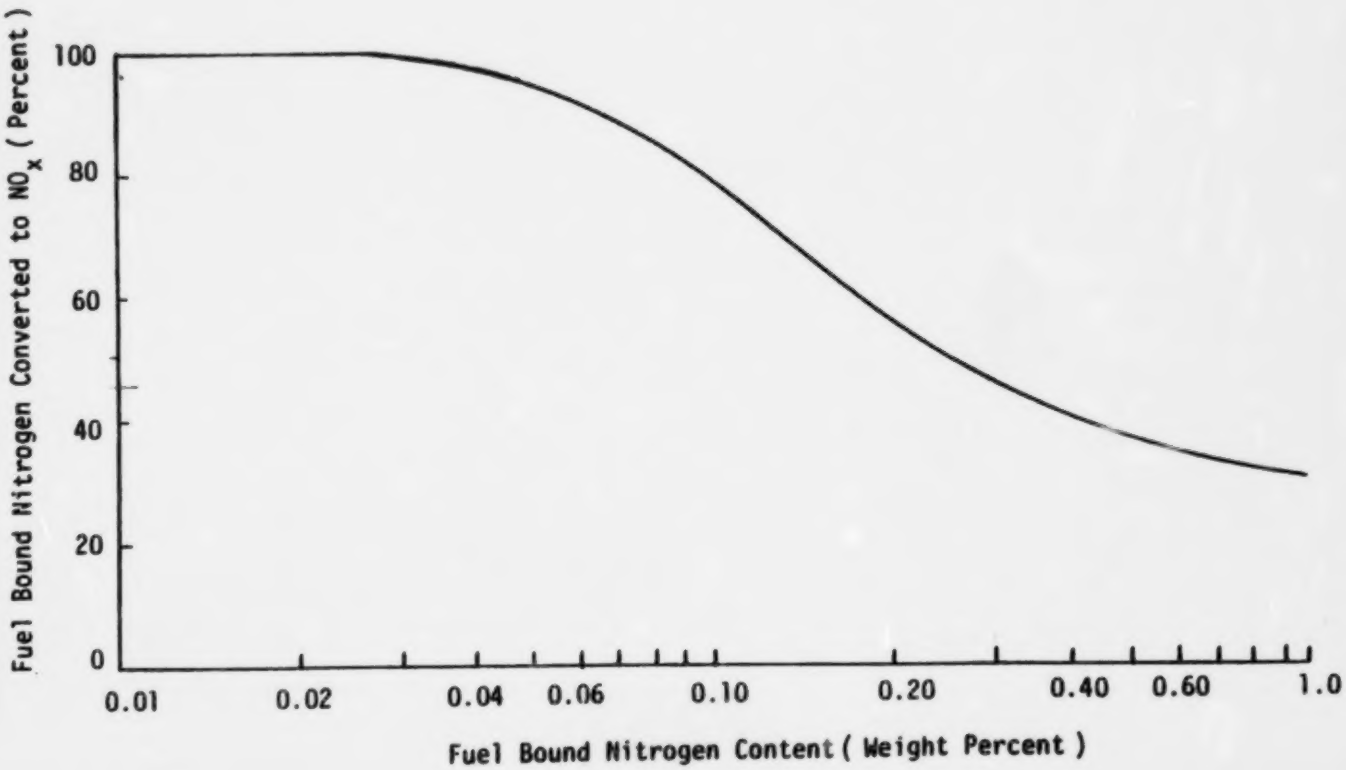

Figure 7-5. Percentage of fuel nitrogen converted to $NO_x$ versus the fuel bound nitrogen content for liquid fuels (turbine firing temperature is 1840°F).[11]

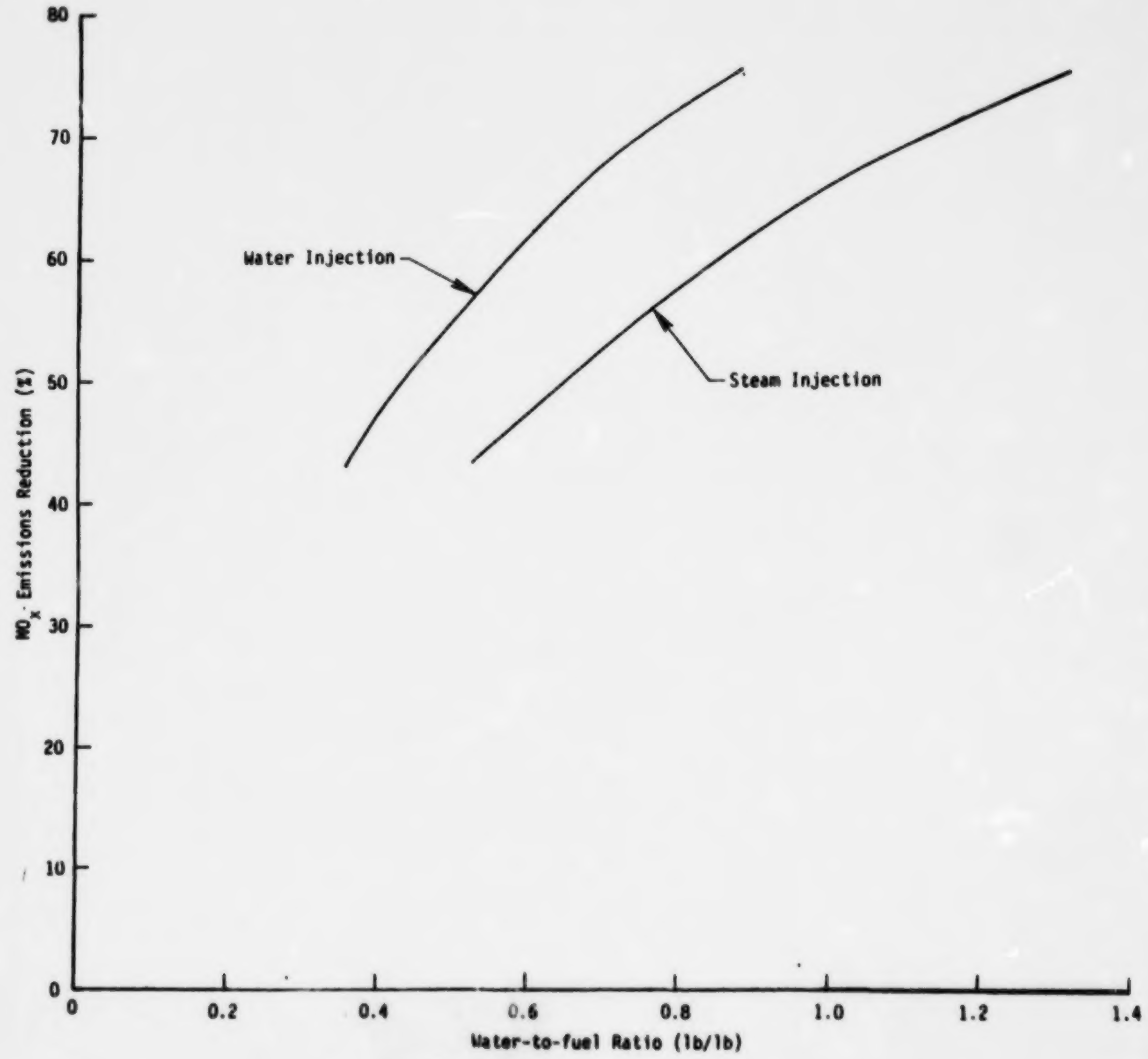

Figure 7-6. $NO_x$ reduction as a function of water-to-fuel ratio for a gas turbine firing natural gas.[13]

The injection of water or steam into the combustor is effective in reducing thermal $NO_x$ emissions, but can actually increase the formation of fuel $NO_x$. Figure 7-7 shows the effect of water injection on $NO_x$ emissions for liquid fuels containing various levels of fuel nitrogen. No data are available on the effects of water or steam injection on nitrogen-containing gaseous fuels.

Another potential method for reducing thermal $NO_x$ emissions from gas turbines firing gasifier product gases is to decrease the residence time during which the combustion gases are maintained at high temperatures. Decreasing the effective combustion gas residence time can be accomplished by adding dilution air to the combustor sooner than with standard combustors. However, decreasing the residence time may result in increased CO and HC emissions unless the combustor design is modified to incorporate better fuel/air mixing and to ensure complete combustion.

Other $NO_x$ control techniques which have been applied to gas turbines firing natural gas or distillate oil include rich-lean combustion and lean-lean combustion. These techniques are not currently applicable to gas turbines firing gasifier product gases, however, due to major design problems such as smoke formation and, where air is limited in the rich zone of the combustor, the need to cool metal surfaces externally instead of using conventional film-cooling techniques.[16]

7.1.3.2 Sulfur Oxides ($SO_x$). Sulfur oxides emissions from gas turbines are directly related to the sulfur content of the fuel, with essentially a 100 percent conversion of fuel sulfur to either $SO_2$ or $SO_3$. In general, a constant fraction of the input sulfur to the combustor is converted to $SO_3$, but this fraction is fuel-specific. For No. 2 distillate oil, experimental data indicate that this fraction is near 3 percent by weight.[17] No data were found to predict the fraction of gasifier product gas sulfur converted to $SO_3$. Depending on the combustor exhaust conditions, some or all of the $SO_3$ formed will be present as $H_2SO_4$.

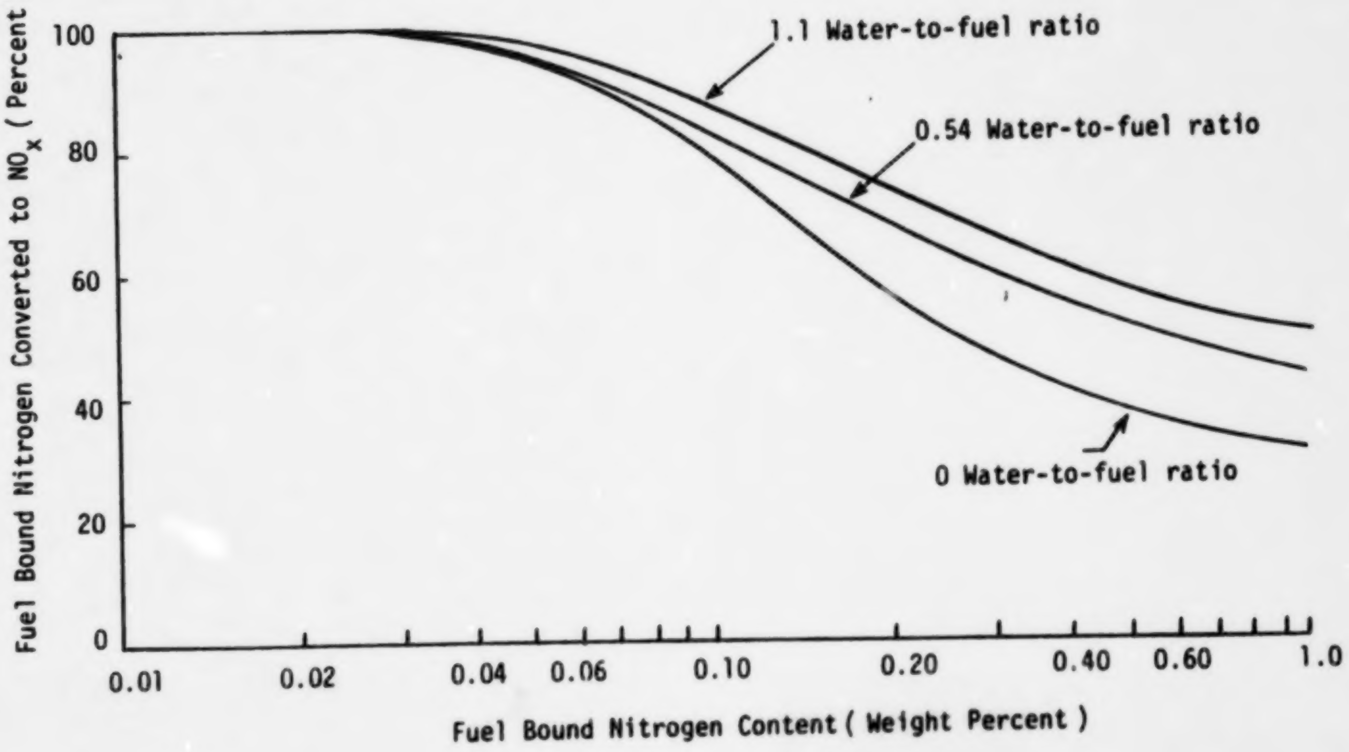

Figure 7-7. Percentage of fuel nitrogen converted to $NO_x$ versus the fuel bound nitrogen content and the water-to-fuel ratio for a turbine firing temperature of 1,840°F.[14]

7.1.3.3 Particulate Matter (PM). Gas turbine exhaust emissions are influenced by the design of the combustion system, fuel properties, and combustor operating conditions. The principal components of particulates are smoke, ash, ambient (i.e., air and injection water) non-combustibles, and erosion and corrosion products.[18] If gasifier product gases are fired in a well-designed, well-operated combustor, the main source of particulate matter will be the non-combustible particulate and other trace contaminants found in the fuel gas.

In addition to contaminants in the fuel, the inlet air and water or steam injection fluids are potential sources of trace metal contaminants which can enter the turbine and cause corrosion and blade deposits. Inlet air contaminants can originate as sea salt aerosols, fly ash, desert sand, soil, dust, fertilizers and carry-over from industrial processes. The water or steam injected for $NO_x$ control can contain alkali or other trace metals unless properly conditioned and handled. It is important to consider these sources when calculating the total contaminant level in the combustion products since it is this level that is critical from a corrosion and deposit standpoint.[19]

7.1.3.4 Carbon Monoxide (CO), Unburned Hydrocarbons (UHC), and Smoke. While $NO_x$, $SO_x$, and PM are the major species of concern from an emissions standpoint, minor components such as CO, UHC, and smoke (i.e., visible emissions) should also be considered, especially to the extent that emission reduction techniques for the major components will effect emissions of minor components.

Carbon monoxide emissions are generally quite low (less than 10 ppmv) for a conventional gas turbine (heavy duty machine series) firing natural gas or distillate oil. Emissions of CO tend to increase, however, as firing temperature is reduced and at lower loads. It is unlikely that a utility gas turbine in a combined cycle plant firing gasifier product gases would operate more than a very short time at low-load conditions where CO emissions would be high. Typical CO emissions from utility gas turbines at or near full load without water injection range from 10 to 200 ppmv.[25]

CO emissions were measured from a Westinghouse test combustor burning medium-Btu gas, as shown in Figure 7-8. All emissions were below 80 ppmv over the range investigated and demonstrated the trends of lower emissions at higher temperatures and higher pressures. CO emissions also appear to be higher for low-Btu gas versus medium-Btu gas combustion. For a General Electric constant cross-sectional combustor operating on low-Btu gas at one-half cycle pressure and low combustor exit temperatures, CO emissions were as high as 4000 ppmv.[27] A variable cross-sectional combustor showed somewhat lower emissions as pictured in Figure 7-9. This figure supports the general trend, however, of lower CO emissions at higher combustor exit temperatures. Two Westinghouse test combustors gave CO emissions of 510 ppmv or less at 88 psia with 136 Btu/scf gas. With lower Btu gas, CO levels over 1,500 ppmv were observed at low exit temperatures.[29] Although there are no NSPS restrictions on CO from utility gas turbines, low CO emissions are desirable from the standpoint of thermal efficiency and safety. CO levels are expected to be below acceptable levels for both low-Btu and medium-Btu product gas combustion if the gas turbine is operated at or near full load and the combustor exit temperature is maintained at high levels, probably above 1600 to 1800°F.

One other factor that can significantly influence CO emissions from a gas turbine is the injection of water or steam to reduce $NO_x$ emissions. The addition of water or steam acts to lower the combustor temperature and can lead to an increase in CO emissions, as illustrated in Figure 7-10 for natural gas combustion. The point at which a sharp increase in CO emissions is observed with increasing water/steam addition is termed the "knee of the curve" and is important in defining the maximum water/steam injection rate for a given combustion system.[33] It should be emphasized that, while the general trend is for higher CO emissions with increased water/steam injection rates, the effect of injection on CO emissions is specific to the machine and injection method and is not predictable in advance.[25]

The tolerance of the combustor to water/steam addition increases as the turbine inlet temperature increases. Thus the use of hot gasifier product gases directly from a gasifier, as opposed to gases that have been cooled by

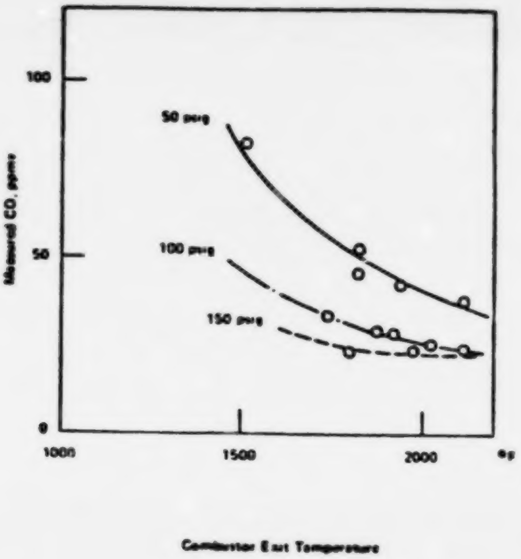

Figure 7-8. CO Emissions from low-Btu gas combustion in a Westinghouse test combustor.[26]

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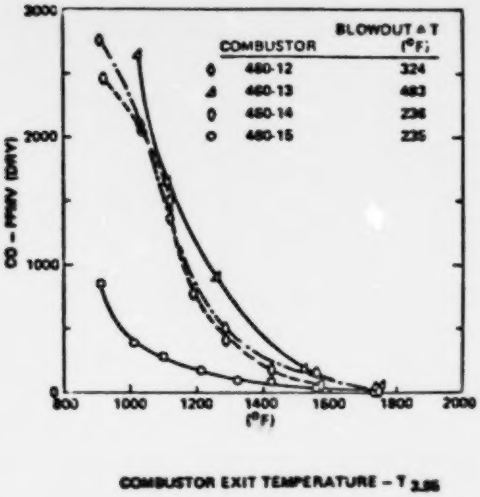

Figure 7-9. CO Emissions from low-Btu gas combustion in a General Electric test combustor.[28]

Source: Reprinted from "Development of an Industrial Gas Turbine Combustion Burning a Variety of Coal-Derived Low-Btu Fuels and Distillates," ASME 79-GT-172, with permission of the publisher, ASME.

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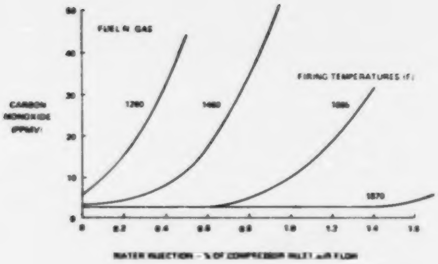

Figure 7-10. Effect of water injection and firing temperature on carbon monoxide emissions.[33]

Source: Reprinted, with permission of the Gas Turbine Reference Library, from Touchton, G. L., et al. (General Electric Company), Emission Performance and Control Techniques for Industrial Gas Turbines. Schenectady, New York. Gas Turbine Reference Library No. GER-2486H. 1982, p. 11.

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water or solvent scrubbing, will allow more water/steam to be added to the gas turbine for $NO_x$ control before CO emissions become a concern.

Like CO, unburned hydrocarbons (UHC) are associated with combustion inefficiency. The data in Figure 7-11a show that UHC emissions from a heavy duty gas turbine firing natural gas or distillate oil decline rapidly as firing temperature increases and are generally less than 10 ppmv at temperatures above 1400°F. Similarly, UHC emissions decrease as turbine load increases (as depicted in Figure 7-11b) and are less than 10 ppmv at all but very low loads for natural gas and distillate oil. For low- and medium-Btu gases, the effect of firing temperature on UHC emissions is illustrated in Figure 7-12. These data show that low- and medium-Btu gases follow the same general trends as natural gas and distillate oil. To ensure UHC emissions below 10 ppmv, the combustor exit temperature for gasifier product gases should be maintained near 1800°F or above. Although no data were found on the effect of load on UHC emissions from low- or medium-Btu gases, the trend is expected to be the same as that shown in Figure 7-11b for natural gas and distillate oil.

Smoke is the visible portion of filterable particulate matter. For liquid fuels, smoke formation is primarily a function of combustor design and the hydrogen content of the fuels. For natural gas, smoke formation is generally negligible over the entire load range.[32] Smoke formation tendencies for gasifier product gases are expected to be similar to those for natural gas under normal gas turbine operating conditions. Smoke formation will likely be a problem only under unusual combustor design/operating conditions such as the rich/lean and lean/lean combustion techniques which are sometimes employed to limit $NO_x$ emissions.

## 7.2 GASIFIER PRODUCT GASES AS GAS TURBINE FUELS

This section discusses the implications of firing gasifier product gases in gas turbines in terms of the impacts on performance, efficiency, emissions, and emissions controls. In particular, the implications of firing medium-Btu gases (from $O_2$-blown gasifier operation) and low-Btu gases

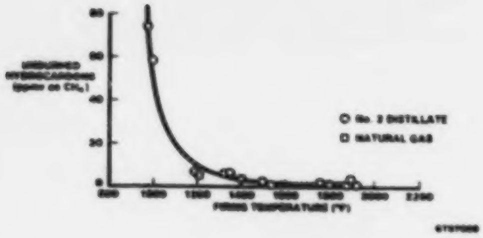

Figure 7-11a. UHC emissions as a function of firing temperature for natural gas and distillate oil.[30]

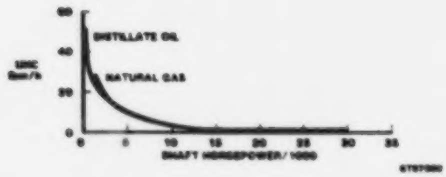

Figure 7-11b. UHC emissions as a function of turbine load for natural gas and distillate oil.[30]

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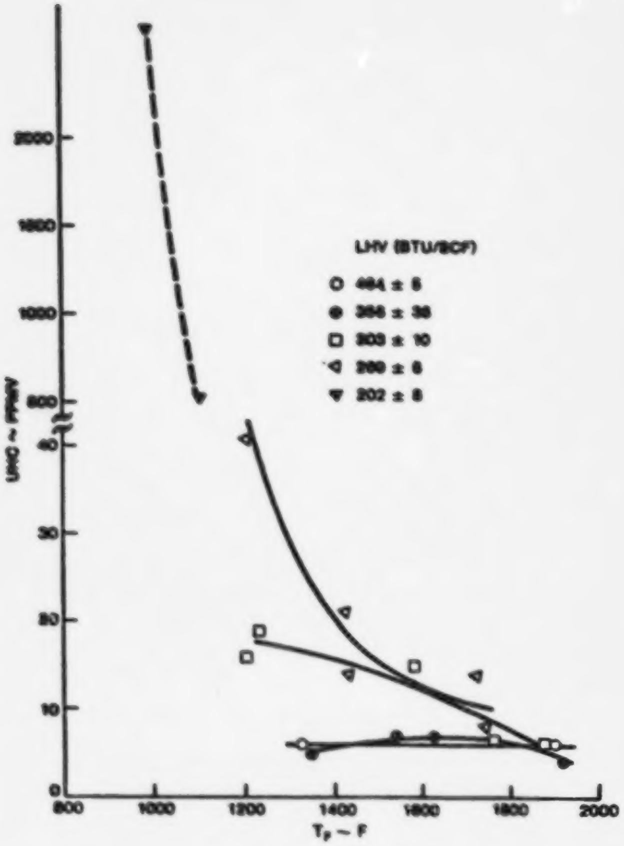

Figure 7-12. UHC emissions as a function of firing temperature for coal-derived gases.[31]

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(from air-blown gasifier operation) produced in entrained-bed slagging gasifiers are examined. The raw synthesis gas from these entrained-bed slagging gasifiers may contain significant amounts of impurities such as $NH_3$, $H_2S$, particulates, and others. As discussed previously, most gasification processes currently include several downstream gas conditioning steps so that the product fuel gas contains negligible amounts of impurities. These typical gas cleaning processes are based primarily on scrubbing, resulting in a product gas at much lower temperatures than the raw synthesis gas. In cases where the gasifier product gas is to be used on site in a gas turbine or combined-cycle application, this reduction in fuel temperature can result in a loss in overall thermal efficiency. Therefore, hot gas cleanup processes or in-situ control of pollutant formation in the gasifier should result in an increased overall thermal efficiency (and possibly reduced costs).

### 7.2.1 Nitrogen Cleanup Requirements

As discussed previously, there are two types of $NO_x$ formed in gas turbine combustors: thermal $NO_x$ and fuel $NO_x$. Thermal $NO_x$ is mostly dependent on the flame temperature in the combustor and is a function of fuel type, firing temperature, combustor pressure, and residence time. Thermal $NO_x$ is the most important contributor to total $NO_x$ emissions in cases where the fuel-bound nitrogen content is low; however, fuel $NO_x$ becomes very important for nitrogen-bearing gaseous fuels such as raw gasifier product gases which may contain significant amounts of $NH_3$ and HCN.

As summarized in Chapter 2, medium-Btu product gases are expected to contain from 0.104 to 0.145 mol percent (dry basis) of $NH_3$ and HCN. Low-Btu product gases generally contain about half the concentration of $NH_3$ and HCN due to the dilution effects of $N_2$ in the fuel gas. Table 7-2 presents calculated values for fuel-$NO_x$ based on these compositions. Table 7-2 shows that maximum fuel-$NO_x$ (based on 100 percent conversion) ranges from 150 to 210 ppmv (dry basis, 15 percent $O_2$ in the exhaust) for medium-Btu gases and from 80 to 115 ppmv for low-Btu gases. Table 7-2 also shows the projected

## TABLE 7-2. ESTIMATED FUEL $NO_x$ AND THERMAL $NO_x$ EMISSIONS FROM GASIFIER PRODUCT GASES

| | Maximum Fuel $NO_x$ ppmv[a,b] | Thermal $NO_x$, ppm[a,c] Combustor Exit Temperature, °F 1200 | 1600 | 2000 |
|---|---|---|---|---|
| Medium-Btu gas | 150 - 210[d] | 50 | 125 | 300 |
| Low-Btu gas | 80 - 115[d,e] | 5 | 10 | 25 |
| Natural Gas | Negligible | 25 | 50 | 150 |

[a] Parts per million volume (dry basis, 15 percent $O_2$ in turbine exhaust gas).

[b] Based on 100 percent conversion of $NH_3$ and HCN to $NO_x$.

[c] See Figure 7-2.

[d] See Tables 2-4 (Texaco Process) and 2-5 for composition of gasifier effluent.

[e] Assumes 60 percent (volume) $N_2$ in gasifier effluent.

thermal-$NO_x$ emissions for medium-Btu and low-Btu gases at various combustor temperatures. The NSPS emission limits (see Section 7.1.2) for total $NO_x$ are about 75 ppmv for electric utility gas turbines larger than 100 million Btu/hour heat input at peak load and about 150 ppmv for gas turbines with rated heat input at peak load between 10 and 100 million Btu/hour. A combined cycle gas turbine firing gasifier product gases, such as the Cool Water facility in California, would fall under the 75 ppmv limit. State regulations, such as California's 40 ppmv limit, may restrict $NO_x$ emissions even further. Thus, it is apparent that the raw gasifier product gases from the gasifier cannot be fired directly in the gas turbine. In order to meet the $NO_x$ emission limitations, reductions in both thermal $NO_x$ and fuel $NO_x$ would have to be achieved since both components are significant. However, the thermal $NO_x$ component of low-Btu gas is very small, such that only a slight reduction in fuel $NO_x$ would be required to meet the existing $NO_x$ emission limitations.

As an example, an electric utility gas turbine with a peak load heat input greater than 100 million Btu/hour operating at a combustor exit temperature of 1600°F and firing medium-Btu coal-derived gas is projected to have total $NO_x$ emissions of approximately 275 to 335 ppmv (125 ppmv thermal $NO_x$ plus 150 to 210 ppmv fuel $NO_x$). Since the $NO_x$ NSPS emission limit for this unit is 75 ppmv, a $NO_x$ emission reduction of 73 to 78 percent would be required to maintain compliance. Even if all the fuel $NO_x$ precursors were removed before combustion, 40 percent of the thermal $NO_x$ would have to be eliminated by combustion modification techniques (most likely water or steam injection) to meet the NSPS limit. By contrast, for the same utility turbine firing a low-Btu product gas, total $NO_x$ emissions are projected to be only 90 to 125 ppmv. Thus elimination of only 19 to 43 percent of the fuel $NO_x$ precursors in the low-Btu gas would enable the unit to meet the NSPS limit without further combustion modification.

For these reasons, in-situ removal and/or hot gas cleanup of $NO_x$ precursors in the gasifier represent very attractive options for low-Btu product gases but are less attractive for medium-Btu product gases. As discussed in Section 7.1.3 and as shown in Table 7-2, increases in temperature have an adverse impact on thermal $NO_x$ emissions, with this impact being significantly greater for medium-Btu gases than for low-Btu gases. Furthermore, the incremental effectiveness of water- or steam-injection in reducing thermal $NO_x$ emissions decreases with increasing water/fuel ratio.

As mentioned above, most operating coal gasification installations include several downstream gas conditioning processes, based primarily on scrubbing, to remove pollutants in the fuel gas. Although these low-temperature cleaning processes may result in a reduced thermal efficiency in cases where the product gas from the gasifier is to be burned on-site, they have the effect of reducing both fuel- and thermal-$NO_x$ emissions. Because the fuel gas is scrubbed, it becomes saturated with water which serves to reduce the combustion flame temperature which, in turn, leads to lower thermal $NO_x$ emissions. In addition, further reduction in thermal-$NO_x$ emissions can be achieved through water- or steam-injection into the combustor. At the Cool Water combined cycle power plant, a $NO_x$ emission limit of 40 ppm is achieved by saturating the fuel gas with water and injecting water into the combustor.[15] Since the fuel gas has been scrubbed to remove fuel-$NO_x$ precursors, there are essentially no fuel-$NO_x$ emissions. It is important to note, however, that any capture of fuel $NO_x$ precursors in the gasifier or hot gas cleanup train will mitigate the extent of thermal $NO_x$ reduction required in the combustor, thereby increasing the efficiency of the turbine.

### 7.2.2 Sulfur Cleanup Requirements

In addition to NSPS limitations which apply to sulfur emissions for gas turbines, turbine metal corrosion considerations limit the total sulfur content of fuel gas to 0.18 mole percent. The information in Table 2-5 for raw gas minor constituents indicates that total sulfur species are expected to range from about 1.25 to 2.24 mole percent for oxygen-blown entrained bed gasifiers. For air-blown operation, the sulfur concentrations will be about half those specified above, or 0.63 to 1.12 mole percent, due to the dilution effect of $N_2$ in the fuel gas.

In order to meet the sulfur corrosion limitations, the total sulfur species must be reduced by 86 to 92 percent in the case of medium-Btu product gas or by 71 to 84 percent in the case of low-Btu product gas. This reduction may be accomplished either by in-situ removal in the gasifier, hot gas cleanup, conventional low-temperature cleanup processes, or a combination of these approaches.

Based on the information presented in Section 4.0, it appears unlikely that this level of sulfur reduction could be accomplished using in-process sulfur controls in the gasifier alone. However, the extent to which sulfur can be captured in the gasifier will reduce the size and expense of downstream sulfur reduction equipment, either for high-temperature or low-temperature processes. For example, for an oxygen-blown entrained-bed gasifier operating at maximum sulfur levels in the product gas (i.e., near 2.24 mole percent), capture of 50 percent of the sulfur by in-process controls would reduce the sulfur reduction burden on downstream equipment from 92 percent to 84 percent. The cost and operational implications of this reduced burden should be significant.

### 7.2.3 Particulate Matter Cleanup Requirements

The degree of PM cleanup required for gas turbine applications is dependent on the type of product gas produced (medium-Btu versus low-Btu gas) and the effect of the materials injected into the gasifier for sulfur and nitrogen control. The PM loading in the raw gas from the Koppers-Totzek (oxygen-blown) entrained-bed gasifier was reported to be 12 to 24 grain/scf.[21] For other entrained-bed gasifiers, typical PM loadings in the raw gas can range up to near 50 grain/scf.[22] The raw gas PM loading is not expected to be greatly influenced by air-blown versus oxygen-blown operation since in both cases superficial gas velocities in the gasifier will be in the entrained flow regime.

The heating value of the product or fuel gas does influence the degree of PM removal required before the gas can be used in a gas turbine, however, as discussed in Section 7.1.2 and illustrated in Table 7-1. Assuming a product gas total PM loading of 25 grain/scf (which is in the middle of the typical range), gas turbine specifications require that this level be reduced to 6.5 ppmw (or near 0.0025 grain/scf) for a medium-Btu gas and 2.3 ppmw (or near 0.001 grain/scf) for a low-Btu gas. The PM removal efficiencies for these two cases correspond to 99.99 percent and 99.996 percent, respectively. If materials such as lime or other sorbents are injected into the gasifier for sulfur and nitrogen species control, the PM loading in the raw gas and PM reduction requirements will be correspondingly higher.

It is obvious that PM reduction equipment must be employed between the gasifier and gas turbine to bring PM loadings down to tolerable levels. In conventional combined-cycle systems, this is typically accomplished by cyclones and wet scrubbers operating in series. Passing the gas through a wet scrubber, however, reduces gas temperatures to the range of 100 to 300°F. To avoid this loss of sensible heat in the product gas stream, hot gas PM cleanup devices may be employed. This equipment may include inertial separators, surface filters, molten salt scrubbers, granular bed filters (GBFs) and electrostatic precipitators (ESPs).

Inertial separators such as cyclones can effectively remove larger size PM (i.e., greater than 6 μm) at temperatures up to 1,500°F but have only low fine particle collection efficiencies.[23] Surface filters, GFBs and ESPs can remove small particles with higher collection efficiencies. Of these, commercially available baghouse filters have not been used above about 550°F. Ceramic fabrics and porous ceramic filters, on the other hand, can operate at temperatures up to 3,000°F but are not commercially available. GBFs have not been used commercially at temperatures about 800°F; ESPs have been tested at 2000°F but have not been applied commercially above approximately 900°F. Although molten salt scrubbers can be used at high temperatures, the entrainment of salt particles in the gas stream and their corrosion effects make them unlikely candidates for gas turbine applications.[24]

Currently there are few data available on the trace metal concentrations in raw gas from entrained-bed gasifiers. The data available indicate that most of the trace metal species are contained in the particulate phase of the raw gas as opposed to the gas-phase.

If commercially-available equipment is used to reduce PM loadings to those specified for the gas turbine, the most likely configuration would be cyclones followed by one or more ESPs. In this case, the fuel gas could be delivered to the gas turbine at or near 900°F. Of the trace metals identified in Table 7-1, none have boiling points below this temperature; thus they should be present in the solid as opposed to vaporized form. By meeting the overall specification on total PM in the product gas, the PM control devices should also reduce the trace metal contaminants below allowable levels. If higher temperature PM control equipment is used, the presence of vaporized trace metals may be a concern for gas turbine applications.

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# 8.0 ASSESSMENT OF GASIFIER PRODUCT GASES AS INDUSTRIAL AND UTILITY BOILER FUELS

## 8.1 INTRODUCTION

The use of gasifier product gases as industrial and utility boiler fuels has been generally assessed by other workers.[1,2] The particular thrust of this section is to examine the implications of using the gaseous products from an entrained-bed gasifier with and without in-process controls as a fuel for new boiler installations or for retrofit use on existing utility and industrial boilers. The use of coal-derived gases will be assessed with regard to their performance as a fuel and with regard to the requirements for meeting applicable emission limits. The boiler modifications that would be required as a result of changing from coal, oil, or natural gas fuel to product gases generated by entrained-bed gasifiers will be reviewed briefly.

After summarizing current practice in the operation of industrial and utility boilers and control of their emissions, attention will be focused on the use of product gases from an entrained-bed gasifier with and without in-process control as described in earlier chapters. The extent of controls needed to meet current emission regulations, in addition to those described in previous chapters as in-process control, will be assessed.

### 8.1.1 Use of Gasifier Product Gas in New Boilers

The heating values (Btu/scf) for natural gas are generally about 3 times those of medium-Btu gas and from 6 to 10 times those of low-Btu gas. The performance of gasifier product gases in boiler applications is generally satisfactory. Although industrial and utility boiler experience is not extensive, it is sufficient to demonstrate the performance of the gasifier product gases for industrial and utility boiler applications.[3,4,5] As discussed earlier, operation of entrained-bed gasifiers in the oxygen-blown mode results in a medium-Btu gas (generally 200 to 400 Btu/scf) while operating in the air-blown mode generates a low-Btu gas (generally 100 to 200 Btu/scf).

Ignition and flame stability have apparently not been problems with the use of low- and medium-Btu gases. As discussed in Section 7.1.3, combustion flame temperature of low-Btu gas is 600 to 900°F lower than that for natural gas. Medium-Btu gas flame temperatures are equal to or higher than that of natural gas.[6] The combustion flame temperature is related to potential $NO_x$ emissions and to radiant heat transfer; the latter is an important consideration in the capacity rating of a boiler.

Fuel gas sulfur levels for clean gasifier product gases differ according to the gas cleaning process and desired degree of cleanup. Product gas sulfur levels may range as high as 1300 ppm and fall as low as 30 ppm for a high efficiency removal system. Reference 44, for example, shows design sulfur ($H_2S$ + COS) levels in the clean gas from a Texaco entrained-bed gasifier to be about 600 ppmv based on Illinois No. 6 coal feed to the gasifier with 4.3 weight percent sulfur. These figures would represent a well-cleaned gas from a high sulfur coal.

$NO_x$ emissions from the combustion of low-Btu and medium-Btu gases are estimated to be similar to those of natural gas (0.12 to 0.23 $lb/10^6$ Btu).[8] The Zeldovich equation presented in Section 7.1.3.1 relates the rate of formation of thermal $NO_x$ to the flame temperature, total pressure, and concentrations of $O_2$, $N_2$ and NO. The equation shows that the rate of thermal $NO_x$ formation increases exponentially with an increase in flame temperature. Therefore medium-Btu gas, having a higher combustion flame temperature than natural gas, would be expected to have higher $NO_x$ emissions than natural gas, while low-$NO_x$ gas, having a lower flame temperature, would produce lower thermal $NO_x$ emissions. Depending on the degree of clean-up, gasifier product gases may also contain $NH_3$ and HCN, which are a source of fuel $NO_x$ when these gases are combusted.

Particulate emissions for cleaned gasifier product gases are similar to those of natural gas, about 4 ng particulate/J (0.01 $lb/10^6$ Btu). Prior to cleaning, however, gasifier product gases may contain significant quantities of PM as discussed below.

### 8.1.2 Retrofit Boiler Modifications

Because the heating values of low- and medium-Btu gases produced from gasifiers are substantially lower than the heating value of natural gas, the gas burners installed in the boilers generally require modification or substitution. Table 8-1 shows combustion properties for natural gas and typical medium- and low-Btu gases. To maintain the same heat input, low-Btu gas requires up to six times the volumetric flow rate compared to natural gas, while medium-Btu gas may require over three times the flow rate of natural gas. Either the pressure drop across the fuel metering device must substantially increase to accommodate the larger flow, or a larger diameter orifice is required. The fuel supply lines and flow control devices may need to be replaced to accommodate the larger flow rates required for medium- or low-Btu gas. On the other hand, combustion air flow requirements for low- and medium-Btu gas are 10 to 22 percent less than natural gas for the same excess air setting and thermal input.[10] Table 8-1 shows the fuel, air, and flue gas flow rates for natural gas, medium- and low-Btu gas.

For medium-Btu gas there may be a net reduction in the volume of flue gas generated per Btu of heat input which may affect the efficiency of heat transfer in the convective section of the boiler.[10] This may adversely affect boiler rating or possibly lower the steam temperature. To compensate, higher excess air levels may be required which may cause an existing boiler to be fan-limited. Flue gas recirculation may also be used to raise the flue gas flow rates, but again this will require additional fan capacity.

## 8.2 INDUSTRIAL AND UTILITY BOILERS

Industrial boilers are used in manufacturing primarily to produce steam or hot water. The steam is generally used either for processing purposes or for generation of electricity. Industrial boilers subject to current New Source Performance Standards (NSPS) are defined as "new, modified, or reconstructed industrial-commercial-institutional steam generating units

## TABLE 8-1. COMBUSTION PROPERTIES FOR TYPICAL HIGH, MEDIUM, AND LOW-BTU GASES[52]

| Property | Natural Gas | Medium-Btu | Low-Btu |
|---|---|---|---|
| Higher Heating Values (Btu/lb) | 22,170 | 5,525 | 2,571 |
| Lower Heating Values (Btu/lb) | 20,050 | 5,150 | 2,365 |
| Ta/f[a], Mass Ratio | 15.9 | 3.23 | 1.49 |
| Ta/f, Volume Ratio | 9.8 | 2.33 | 1.22 |
| Theoretical Flame Temperature (°F) | 3,480-3,700 | 3,300-3,800 | 2,800-3,500 |
| Vol. Fuel Gas scf/$10^6$ Btu[b] | 961/1,062 | 3,301/3,542 | 6,211/6,751 |
| Vol. Air, scf/$10^6$ Btu[b] | 10,830/11,970 | 9,060/9,720 | 9,418/10,240 |
| Vol. Flue Gas, scf/$10^6$ Btu[b] | 11,870/13,180 | 11,024/11,830 | 14,324/15,570 |
| lb Flue Gas/$10^6$ Btu[b] | 870/962 | 871/935 | 1,107/1,203 |
| Molecular Weight Flue Gas[b] | 27.8 | 30.0 | 29.3 |

[a] Ta/f = theoretical air/fuel ratio for stoichiometric combustion.

[b] 3 Percent excess oxygen (higher heating value basis/lower heating value basis).

capable of combusting more than 29 MW (100 million Btu/hour) heat input." Industrial boilers cover a wide range of sizes with some units as large as 200 MW heat input (700 million Btu/hour) of fossil fuel.

Utility boilers are steam generating units whose function is primarily to make electricity for sale to the general public. Utility boilers subject to current NSPS are defined as "new, modified, or reconstructed electric utility steam generating units capable of combusting more than 73 MW heat input (250 million Btu/hr) of fossil fuel."

### 8.2.1 Emissions From Boilers

Emissions of primary concern from boilers combusting gasifier product gas are particulate matter (PM), sulfur oxides ($SO_x$), and nitrogen oxides ($NO_x$). Emissions of secondary concern are carbon monoxide (CO), hydrocarbons (HC), and trace elements.

For boilers burning gasifier product gas, the primary source of PM emissions will be the PM loading of the fuel gas itself. Under efficient combustion conditions, negligible amounts of soot from unburned carbon are expected to be formed. Thus the PM loading of boiler flue gas (on a heat input basis) will be the same as the fuel gas (less any small amounts of PM that settle out as bottom ash or collect on boiler surfaces).

Uncontrolled emissions of $SO_2$ will depend almost exclusively on the sulfur content of the gasifier product gas. Although some $SO_2$ is normally retained in the bottom ash and fly ash from alkaline ash coal, the PM loading of the fuel gas delivered to the boiler will be so low (due to burner restrictions) that PM alkalinity will have little or no effect. Thus all of the sulfur values in the fuel gas are expected to report to $SO_2$ in the flue gas.

Oxides of nitrogen result from the oxidation of atmospheric nitrogen during the combustion process (thermal $NO_x$), or from the nitrogen content of the fuel itself (fuel-bound nitrogen). For natural gas and distillate oil, nearly all $NO_x$ formed is thermal $NO_x$. For residual oil and coal with high nitrogen contents, the majority of the $NO_x$ may derive from fuel-bound nitrogen. For gasifier product gas, ammonia and HCN in the gas phase are the primary sources of fuel-bound $NO_x$.

$NO_x$ emissions are dependent on the combustion conditions in the furnace. Primary variables affecting the formation rate of $NO_x$ are (1) the nitrogen ($N_2$, and N) concentration, (2) the local flame oxygen concentration ($O_2$ and O), (3) the maximum flame temperature, (4) the temperature profiles, and (5) the hydrodynamic and mixing profiles. Control of $NO_x$ emissions depends on the control that can be exercised on the variables listed, and is described in more detail below.

CO and HC emissions are related primarily to the combustion efficiency of the fuel. These emissions are inversely proportional to the air/fuel ratio. In the present study of the use of gas from entrained-bed gasifiers, these emissions are expected to be of minor concern as long as the combustion in the boiler is sufficiently efficient to prevent the emission of PM in the form of soot.

### 8.2.2 Applicable Emission Limits for Boilers Firing Gasifier Product Gases

In assessing the suitability of low- or medium-Btu gas from entrained-bed gasifier units it is necessary to know the applicable emission limits. For the current study of in-process control for entrained-bed gasifiers, one must also consider erosive and/or corrosive properties of the products from the gasifier. For example, if lime or other alkaline oxides used to reduce potential $NO_x$ and $SO_x$ emissions are present in the product gas along with a significant amount of moisture, a corrosive condition will result and stress corrosion cracking of carbon steel and stainless steel may be a concern. Also, the addition of CaO as an in-process control device may increase the particulate loading of the fuel gas, including CaS and unreacted CaO particles, resulting in an erosive condition. The distribution of CaO and CaS between gasifier slag and product gas PM is not certain; more data are needed in this area.

In the gasifier systems studied in Sections 3 and 4, CaO-to-sulfur molar ratios were generally in the range of 3.0. If a significant fraction of this added CaO exits the gasifier with the product gas, as opposed to the slag stream, then particulate matter control out of the gasifier would be required before the gasification products could be introduced into a burner. This is due to the erosion and fouling potential of the suspended particulate on the burner surfaces and on the boiler tube walls in the combustion region of the boiler. In addition, high particulate loading in the boiler may result in fouling of the heat exchanger surfaces because of settling of CaO, slag, ash and char on surfaces.

Table 8-2 summarizes New Source Performance Standards for new, modified, or reconstructed coal-fired industrial and utility boilers. These standards will also apply to a gasifier-boiler combined system where both the gasifier and boiler are located at the same site. It is important to note that, for these systems, emission limits and percent reduction requirements are based on the heat input and sulfur content of the coal fed to the gasifier and not the fuel gas fired in the boiler.

For particulate matter, the NSPS emission limits are 13 ng/J (0.03 lb/million Btu coal) for utility boilers and 22 ng/J (0.05 lb/million Btu coal ) for industrial boilers. These PM loading limits would also apply to the fuel gas fed to the boiler burners, unless erosion or plugging of the burner is an additional consideration. A burner consisting of a straight pipe or tube which feeds the fuel into the combustion zone would not tend to plug or fail. Some burner designs, however, have gas nozzles or orifices for which the particulate loading specifications are less than 0.015 grains/scf.[53] Moreover, if the burners have gas igniters, the maximum recommended particulate loading is 0.005 grains/scf because the nozzle or orifice size in the ignitor is smaller than in the burner and would tend to plug with particulate matter.

While it is clear that new industrial and utlity boilers which combust gas from an entrained-bed gasifier will be subject to the applicable NSPS, these emission limitations will also apply, in most cases, to retrofit units where natural gas or oil is replaced by coal as the feed material. For the retrofit case, an existing natural gas- or oil-fired boiler would be replaced with a gasifier-boiler system operating on coal. Due to the

TABLE 8-2. NEW SOURCE PERFORMANCE STANDARDS FOR COAL-FIRED BOILERS[d]

| | Utility[a] | Industrial[b] |
|---|---|---|
| PM | 13 ng/J (0.03 lb/million Btu) | 22 ng/J (0.05 lb/million Btu)[b] |
| Opacity | 20 Percent (6-minute average) | 20 Percent (6 minute average)[b] |
| $NO_x$ | 210 ng/J (0.50 lb/million Btu) | 301 ng/J (0.70 lb/million Btu)[b] for pulverized coal<br>258 ng/J (0.60 lb/million Btu) for a spreader stoker coal-fired unit.<br>215 ng/J (0.50 lb/million Btu) for a mass-feed stoker coal-fired steam generator |
| $SO_2$ | Equal to or less than:<br>(1) 520 ng/J (1.2 lb/million Btu) heat input and 10 percent of the potential combustion concentration (90 percent reduction), or<br>(2) 30 percent of the potential combustion concentration (70 percent reduction), when emissions are less than 260 ng/J (0.60 lb/million Btu) heat input. | 520 ng/J (1.20 lb/million Btu)[c] |

[a] Electric utility steam generating unit capable of combusting more than 73 MW (250 million Btu/hour) heat input from fossil fuel. Standards are for solid and solid-derived fuels (e.g., gas from coal gasification units).

[b] Standards for industrial-commercial-institutional steam generators having a capacity of more than 29 MW (100 million Btu/hr) heat input which fire coal or coal-derived fuels.

[c] Standard for industrial-commercial-institutional steam generators having a capacity of more than 73 MW (250 million Btu/hr) heat input which fire coal or coal-derived fuels. Standards for smaller steam generators are currently under development.

[d] Emission limits and percent reduction requirements are based on the heat input and sulfur content of the coal fed to the gasifier and not the fuel gas fired in the boiler.

anticipated expense of this conversion, most boilers will fall into the "modified" or "reconstructed" category and hence will also be subject to NSPS limits. Those retrofit boilers which do not fall into these categories will be subject to State Implementation Plan (SIP) limits which, for many states, have been revised to match the applicable NSPS. For these reasons, the NSPS limits for PM, $NO_x$, and $SO_2$ are representative of the emission restrictions which both new and retrofit gasifier-boiler systems will be required to meet.

It will be observed that for PM, $NO_x$, and $SO_2$ emissions, the utility boiler standards are more stringent than the corresponding standards for industrial boilers. In calculating the 70 to 90 percent reduction of potential $SO_2$ emissions for utility boilers, the percent reduction includes all types of $SO_2$ and sulfur removal technology including coal treatment and the coal gasification step. Therefore the amount of sulfur removed in the entrained-bed gasifier qualifies as part of the overall required percent reduction.

In the case of the industrial boiler $NO_x$ standard, the emission limit is tied to the type of boiler in which the coal is combusted. For a gasifier-boiler system, however, none of these boiler types strictly apply. This situation is not addressed in the regulation and hence would be left to determination on a case-by-case basis. Since pulverized coal boilers predominate among larger boiler installations (i.e., above 400 million Btu/hr heat input) and a combined gasifier-boiler system would most likely be built in lieu of a large boiler, the 0.7 lb $NO_x$/million Btu coal will be assumed as the applicable limit for these systems.

A brief review will be given of $NO_x$, $SO_x$ and PM control options available to the boiler operator in addition to in-process control within the gasifier.

### 8.2.3. Boiler Emission Control Operation

8.2.3.1 Precombustion Fuel Modifications. Fuel modifications prior to complete combustion of the fuel are designed to decrease the emissions of

$NO_x$, $SO_x$, and particulate material. For gaseous fuels, scrubbing with solvents that primarily remove $SO_2$, $H_2S$, COS, HCN, $NO_2$, and particulate material are widely used in the natural gas industry and elsewhere.

Current coal gasification systems do not use in-process control techniques and hence require gas cleaning systems downstream of the gasifier for $H_2S$, $CO_2$, COS, $SO_2$, HCN, $NO_x$, $NH_3$, and ash removal. Twenty-four acid gas treatment systems are listed in one reference.[28] The acid gas treatment processes include treatments for removal of $CO_2$, $H_2S$, COS, $CS_2$, thiophenes, and mercaptans. Other processes are available for ammonia removal. The resulting gas is a clean fuel which is essentially free of particulates and has very little fuel sulfur or fuel nitrogen which are precursors to $NO_x$, $SO_x$, and PM emissions. Hot gas cleanup processes have been studied particularly for use with coal gasification and combustion processes.[29,30] Particulate matter and $H_2S$ are the primary targets for removal from the gas phase in these processes. A number of hot gas cleanup processes use molten salts, while others employ solid adsorbents or reactants.

The potential for thermal $NO_x$ formation in the combustion of the low- or medium-Btu gas is still significant because of the peak combustion temperatures involved in industrial and utility boilers, and because air, with 79 percent nitrogen content, is used as the oxidant feed to the boiler. The overall rate of thermal $NO_x$ formation in the combustor is directly proportional to the $N_2$ concentration.[15] Control of $NO_x$ emissions from boilers is accomplished primarily by staged combustion, use of less excess air, and flue gas recirculation, as discussed in Section 8.3.2.

8.2.3.2 Combustion Modification. A number of boiler combustion modification techniques have been found useful in controlling certain undesirable emissions. The most successful $NO_x$ control (except for precombustion fuel nitrogen removal of heavy oils and coal) is combustion modification.[16,17,18] Some of the more commonly used methods of combustion modification for $NO_x$ control are:

- staged combustion by addition of air in different zones of the combustor,
- lower excess air,
- flue gas recirculation,
- suppression of convective mixing of air in the secondary combustion zone,
- reduction of the peak temperature in the primary combustion zone by not preheating the primary combustion air (or oxygen),
- reduction of the peak temperature in the primary combustion zone by the addition of water to the fuel.

Other combustion modification techniques include staged addition of ammonia as in Exxon's Thermal DeNO$_x$ Process[19] and staged addition of small jets of oxygen.[20]

Another control option that may be classified as a combustion modification is the use of additives with the fuel that change the reactions occurring in the flame zones so as to control or reduce NO$_x$, SO$_x$, and/or particulate emissions. The limestone injection multistage burner (LIMB) process combines a multistage burner with the addition of finely divided limestone or CaO in a slurry of powdered coal to help control SO$_x$ and possibly NO$_x$ emissions from boilers.[21,22] As outlined in Chapter 5, such an addition of CaO or other alkaline metal oxides to an entrained-bed gasifier is proposed as an in-process control of gasifier emissions. Reactions of CaO in the gasifier with $H_2S$ and with HCN result in CaS and CaNCN being discharged from the gasifier in the solid phase, thus helping to control the SO$_x$ and NO$_x$ precursors in the gaseous product from the gasifier.

8.2.3.3 Post Combustion Control. A number of post combustion controls are available which collect, adsorb, absorb, or react with undesirable emissions.

For particulate matter, control options are:

- cyclone separators,
- multicyclone separators,
- gravel bed filters,
- wet scrubbers,
- electrostatic precipitators, and
- baghouse filters.

Frequently combinations of these control techniques are used together (generally in series) such as a cyclone separator followed by an electrostatic precipitator or baghouse. Wet scrubbers can remove more than particulate from the gas phase including $NH_3$, $H_2S$, $SO_2$ and/or $NO_x$ and HCN. The scrubber water absorbing such materials would need to undergo some cleanup processes before it can be discharged to the environment, or recycled to the scrubbing unit in contact with the raw gas from the gasifier.

Flue gas desulfurization systems have been in use and under development for a number of years.[24,25,26,27] Post-combustion control of $NO_x$ has been developed extensively in Japan.[31,32] The majority of these processes involve catalytic reduction of $NO_x$ to nitrogen.

## 8.3 COMBUSTION OF GASIFIER PRODUCT GASES IN BOILERS

Although experience on the use of low- and medium-Btu gas produced by coal-fed gasifiers in industrial and utility boilers is not extensive, there is long-term experience of the use of low heat content gaseous fuels.[3,33] Low heating value gases (40 to 600 Btu/scf) that have been used in industrial and utility applications include coke-oven gas, refinery regenerator waste gas and blast furnace gas. The composition of low- and medium-Btu gasifier product gas is highly variable and depends on such factors as coal type, gasifier type, gasifier operating conditions and the extent of gas cleaning.

Caterpillar Tractor Company has used a low-Btu gas to fire several heat treating furnaces since 1979.[34,35] A 170 MW combined cycle electric power unit uses a coal gasification unit and a pressurized (10 atm) boiler to drive a 96 MW steam turbine generator. A larger (400 MW) unit has been designed.[36]

Allis-Chalmers has operating experience with turbines and boilers using KILnGAS, which is a low-Btu gas generated by a kiln-type gasifier.[54,55] Allis-Chalmers, the Electric Power Research Institute (EPRI), a number of utilities, and the State of Illinois are conducting a KILnGAS demonstration program at the Wood River Station of Illinois Power Company scheduled to commence in early 1986.[56] Low-Btu KILnGAS will be tested as a fuel in a utility boiler at the Wood River Station.

This section compares the use of natural gas with use of low- and medium-Btu gases in utility and industrial boilers. Three types of gasifier products are considered: (1) raw synthesis gases exiting directly from an entrained-bed gasifier, (2) synthesis gas produced by a gasifier with the in-process controls proposed in Chapter 5, and (3) gases cleaned by conventional methods in coal gasification plants.

### 8.3.1 Particulate Matter Cleanup Requirements

As indicated in Section 7.2.3, anticipated particulate loadings for an oxygen-blown entrained-bed gasifier range from 12 to 50 grains/scf; this loading is not expected to be greatly influenced by air-blown versus oxygen-blown operation since in both cases superficial gas velocities in the gasifier will be in the entrained flow regime. The NSPS particulate matter standards for utility boilers and industrial boilers are 0.03 lb/million Btu and 0.05 lb/million Btu, respectively.

Boilers equipped with gas nozzles (gas spuds) with one or more orifices have specifications on gaseous fuels of particulate matter loadings less than 0.015 grains/scf[65] to prevent fouling or clogging of the orifice(s). Frequently gas boilers have gas ignitors (or pilot lights) which require a gas fuel particulate matter loading of no more than 0.005 grains/scf. This latter equipment specification would be equivalent to a flue gas loading of approximately 0.005 lb/million Btu for air-blown gasifier operation and

0.011 lb/million Btu for oxygen-blown gasifier operation. The flue gas loading for the 0.015 grains/scf specification would be three times the previous numbers.

It is apparent that the gas burner PM loading specifications are more stringent than the NSPS limits and hence will be the controlling factor when designing PM reduction equipment. Assuming a raw gas PM loading of 25 grains/scf (which is in the middle of the typical range), gas burner specifications would require PM removal efficiencies of 99.94 percent for the 0.015 grain/scf limit and 99.98 percent for the 0.005 grain/scf limit. If materials such as lime or other sorbents are injected into the gasifier for sulfur and nitrogen species control, the PM loading in the gasifier product gas and PM reduction requirements may be higher, depending on the amount of sorbent entrained in the product gas. At this time, no data are available on the distribution of injected sorbent between slag and product gas PM.

Particulate matter control devices that could be used in this application include cyclone separators, gravel bed filters and electrostatic precipitators for hot gases and wet scrubbers and baghouse filters for cooled gas. The performance capabilities of these devices are discussed in Section 7.2.3.

### 8.3.2 Nitrogen Cleanup Requirements

For fuels having no fuel-bound nitrogen, NO is formed during combustion by the Zeldovich reactions and others; it is emitted as NO, $NO_2$, $N_2O$, etc., and is termed "thermal $NO_x$." When solid fossil fuels such as coal or lignite having fuel-bound nitrogen in their makeup are gasified, the primary gasification products containing nitrogen are HCN, $NH_3$, NO, $NO_2$, and $N_2$.

Very little experimental data are available on the distribution of the fuel-bound nitrogen gasification products, including char, except from experimental and pilot scale apparatus.[45,58] A study has recently been conducted on an industrial boiler burning low-Btu gas. The study reported the distribution of NO, HCN, $NH_3$, and $N_2$ in the flue gas.[57]

Gas from an entrained-flow gasifier could also contain char in the form of particulate matter which, depending on PM loading and nitrogen content, would be an important source of fuel $NO_x$ formation.[59,60] However, as indicated in the discussion above, product gas PM loadings must be reduced to the range of 0.005 to 0.015 grain/scf to meet gas burner specifications. Based on data from a commercial Texaco oxygen-blown gasifier, the nitrogen content of entrained PM approximates that of the feed coal.[66] Thus even for a worst case scenario where 5 weight percent nitrogen coal is fed to an air-blown gasifier to produce a gas whose PM loading is subsequently reduced to 0.015 grain/scf before combustion, the $NO_x$ contribution of the PM would be only about 0.002 lb/million Btu (assuming all the PM nitrogen is converted to $NO_x$). Thus for cases where product gas PM loading is reduced prior to combustion, char nitrogen will not be a significant contributor to boiler $NO_x$ emissions.

Table 2-5 gives concentration ranges for $NH_3$ and HCN, but no data are available for NO in the raw gas. Work conducted by Price, et al.[45] and Highsmith, et al.[67] in a laboratory-scale entrained-flow gasifier showed significant NO (and $SO_2$) concentrations in the raw exit gas even though the gasifier was operating under overall fuel-rich conditions (i.e., oxygen/coal equal to 0.91; steam/coal equal to 0.27). Further analyses of the data, however, indicated that, although NO (and $SO_2$) are formed in the early regions of the gasifier, if sufficient residence time exists in the entrained reactor virtually all the NO (and $SO_2$) is reduced to $N_2$, $NH_3$, $H_2S$, and other fuel-rich species. Thus little or no $NO_x$ is expected in the exit gas from a commercial entrained-bed gasifer operating with sufficient residence time to ensure high carbon conversion.

For purposes of the present analysis, the concentrations given in Table 2-5 will be used as representative values for $NH_3$ and HCN. Table 2-5 indicates that in the oxidized state (i.e., upon complete oxidation) the $NH_3$ and HCN content of the gas leaving the gasifier would result in $NO_x$ concentrations ranging from 0.49 $lb/10^6$ Btu to 0.58 $lb/10^6$ Btu of product gas from an oxygen-blown gasifier. As discussed in Section 8.2.2, the emission limits for a gasifier-boiler system are based on the coal heat input to the gasifier, not the fuel gas heat input to the boiler. For the Texaco entrained-bed gasifier, theoretical material balances developed by Fluor Engineers indicate that there 0.996 Btu of gas will be produced per Btu of coal for oxygen-blown operation and 0.782 Btu of gas per Btu of coal for air-blown operation.[44] These values will be taken as representative for entrained-bed gasifiers. Thus, in the fully oxidized state, the $NH_3$ and HCN in gasifier product gas would result in $NO_x$ emissions of 0.49 to 0.58 $lb/10^6$ Btu coal for oyxgen-blown operation and 0.38 to 0.45 $lb/10^6$ Btu coal for air-blown operation. These figures represent fuel $NO_x$ only and do not account for any thermal $NO_x$ that would be generated in the boiler.

$NO_x$ emissions data from a boiler burning gasifier product gases were obtained in tests conducted by the Riley Stoker Corporation.[61] These tests took place in a furnace measuring 0.91x0.68x1.6 m (36x27x62 in.). The burner was a sealed register type unit similar to those used in utility and industrial boilers. Most of the Riley Stoker data applied to combustion of low-Btu gas (140-170 Btu/scf) with ammonia concentrations of 280-270 ppmv. One test was conducted using medium-Btu gas (270 Btu/scf) containing 1170 ppmv ammonia. The results of these tests are shown in Figures 8-1 and 8-2. In order to identify the quantity of $NO_x$ attributable to thermal fixation, tests were conducted using low $NH_3$ (11-43 ppmv) concentrations. At 6 percent excess oxygen, thermal $NO_x$ emissions were around 1.0 ppmv (dry, at 3 percent $O_2$) per $KW_T$ heat input to the test furnace. At 4 percent excess oxygen, thermal $NO_x$ was 0.85 ppmv per $KW_T$.

The resulting thermal $NO_x$ emissions (from the low $NH_3$ runs) were 63 to 120 ng (as $NO_2$) per J (0.15-0.28 $lb/10^6$ Btu) of fuel gas.[61] By subtracting these thermal $NO_x$ emissions from the total $NO_x$ emissions, Riley Stoker was able to estimate the fuel-bound $NO_x$ emissions. These are presented in Figure 8-3.

Based on the Riley Stoker results, Figures 8-4 and 8-5 were derived. These are important results because they show the proportion of ammonia in gasifier product gas that is converted to $NO_x$. The higher the concentration of ammonia in the fuel gas, the lower the conversion of the ammonia to $NO_x$.

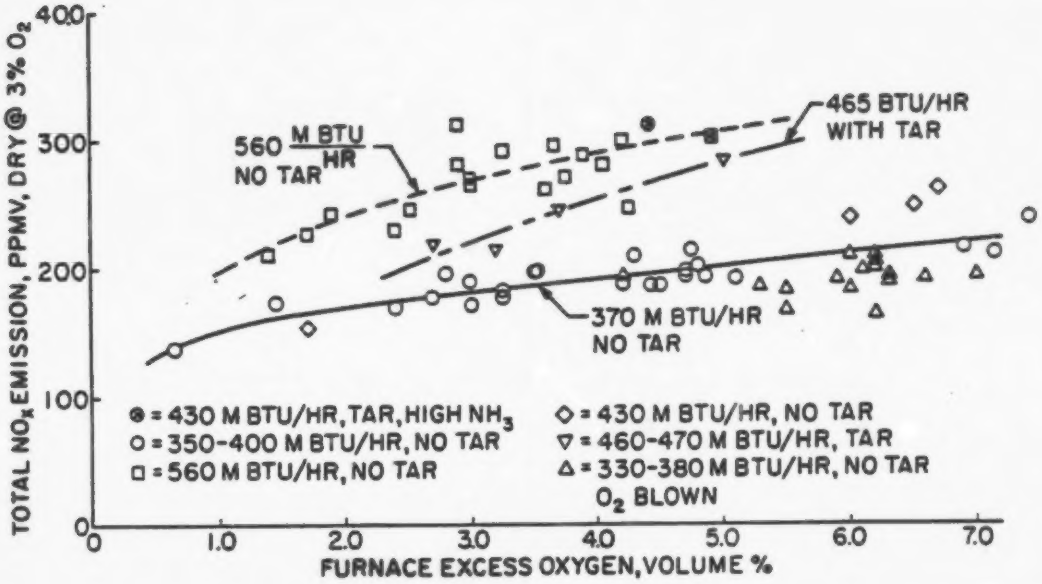

Figure 8-1. $NO_x$ emission data for coal-derived syngas combustion.

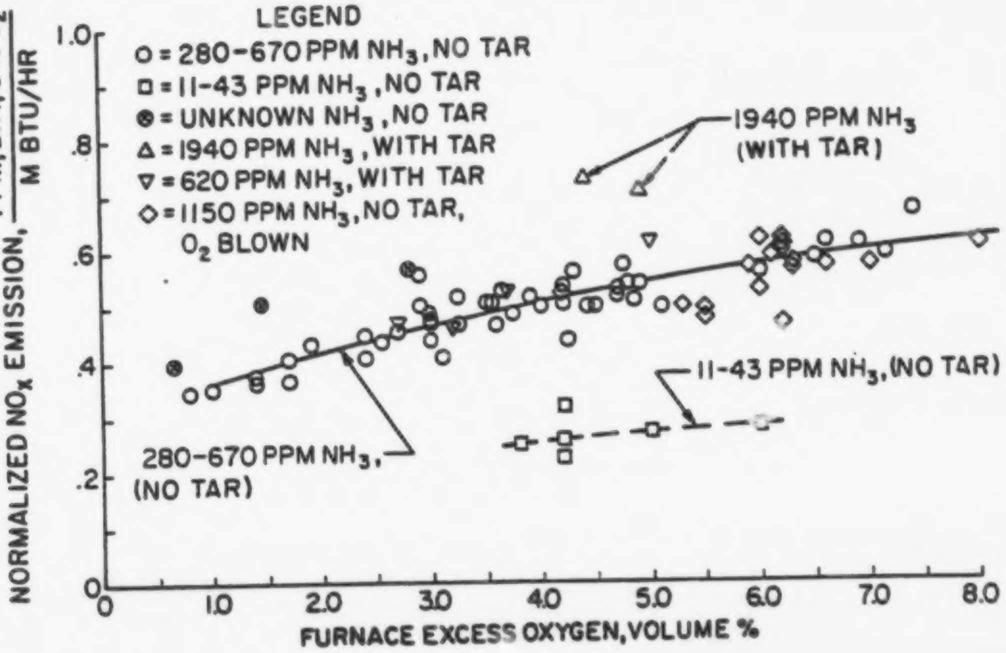

Figure 8-2. $NO_x$ emission data (normalized with respect to furnace heat input) for coal-derived syngas combustion.[61]

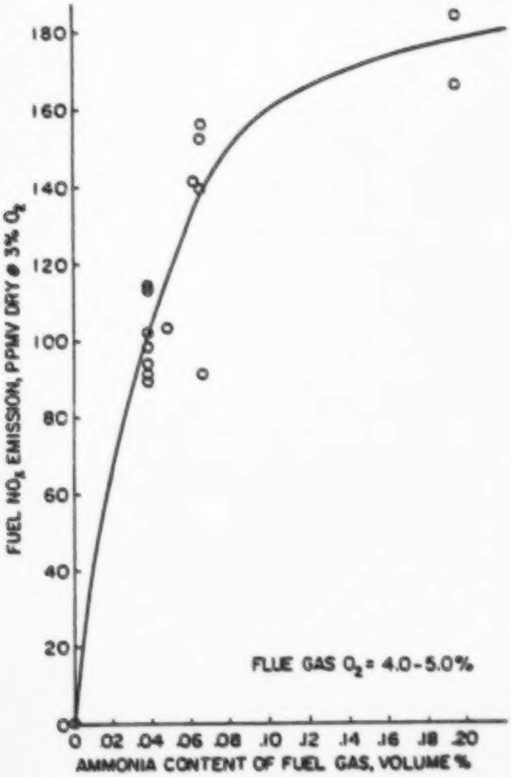

Figure 8-3. Fuel NO$_x$ emissions for gasifier product gas combustion.[62]

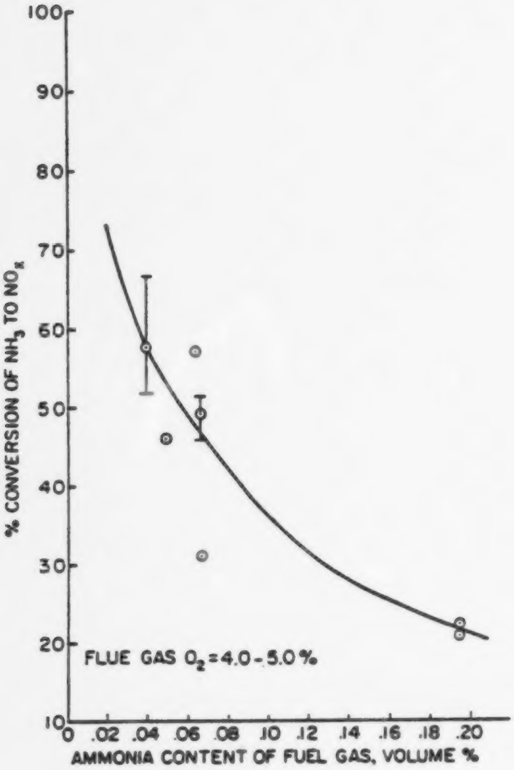

Figure 8-4. Conversion of $NH_3$ to $NO_x$ for gasifier product gas combustion.[62]

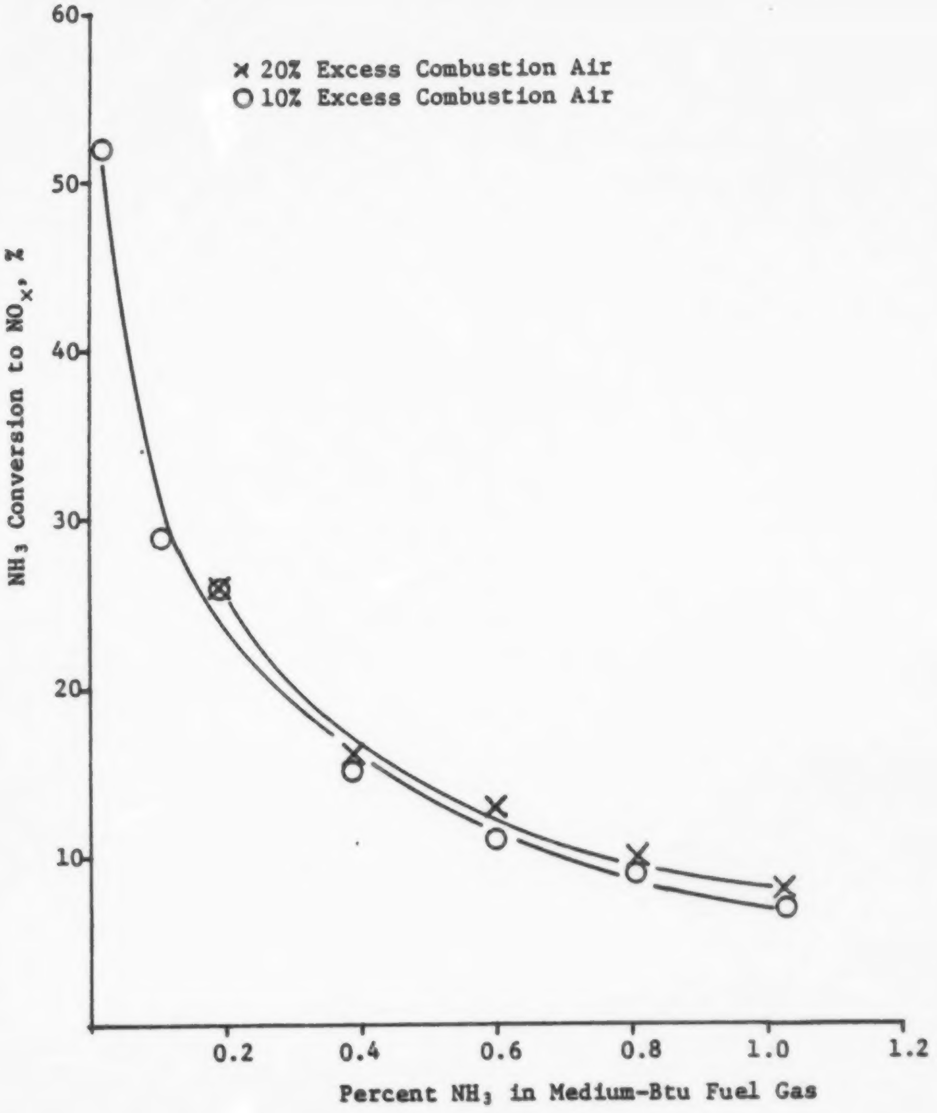

Figure 8-5. Conversion of $NH_3$ to $NO_x$ for medium-Btu gas combustion using baffle burner.[62]

The reaction mechanisms for the combustion of HCN and $NH_3$[59,60] indicate that $NH_3$ can oxidize to NO or to $N_2$.

The Institute of Gas Technology (IGT) also conducted tests[62] to show the effect of $NH_3$ on $NO_x$ emissions. The IGT studies included baseline tests on both clean product gas and natural gas. The IGT baseline tests are given in Table 8-3. As indicated in this study, thermal $NO_x$ emissions for medium-Btu gas (202 to 267 Btu/scf) are 47 to 86 percent of those for natural gas combustion, while thermal $NO_x$ emissions for clean low-Btu gas (149 to 159 Btu/scf) are from 32 to 80 percent of those for natural gas combustion.

The IGT tests show baseline $NO_x$ readings about one sixth those of the Riley Stoker "low $NH_3$" $NO_x$ readings. The higher $NO_x$ readings of the Riley Stoker "low $NH_3$" tests are a result of the 11-43 ppmv of $NH_3$. Table 8-4 indicates the magnitude of the effect of various amounts of $NH_3$ in the gas phase on the $NO_x$ concentration in the flue gas. Table 8-4 also shows data for natural gas and for char and tar added to gasifier product gas.

The reduction of $NO_x$ by $NH_3$ is a widely recognized reaction and is, in fact, the basis of Exxon's Thermal De$NO_x$ process. In this combustion modification process, $NH_3$ is injected into boiler flue gas in the higher temperature regions of the furnace. It is not surprising, therefore, that $NH_3$ would also act to reduce $NO_x$ in a boiler firing fuel gas with significant $NH_3$ concentrations. The extent of $NO_x$ reduction will depend on the combustion conditions and the competition between $O_2$ and $NO_x$ as reactants for available $NH_3$.

The data plotted in Figure 8-4 indicate that only 35 percent of the $NH_3$ in the medium-Btu product gas represented in Table 2-5 (with approximately 0.10 volume percent $NH_3$) would be converted to $NO_x$ in the boiler. For air-blown operation (with approximately 0.05 volume percent $NH_3$), the conversion of $NH_3$ to $NO_x$ would be near 55 percent. Applying these conversion factors to the values in Table 2-5 results in predicted fuel $NO_x$ emissions of 0.22 to 0.31 lb/$10^6$ Btu coal for oxygen-blown gasifier operation and 0.24 to 0.30 lb/$10^6$ Btu coal for air-blown operation. Table 8-5 lists projected fuel $NO_x$ and thermal $NO_x$ emissions for boilers combusting natural gas, two medium-Btu product gases, and a low-Btu product

TABLE 8-3. SUMMARY OF IGT BASELINE COMBUSTION TESTS[a]

| Burner Used | Fuel | Fuel Temperature, °C(°F) | $NO_x$ Emissions,[b] ng/J (lb/$10^6$ Btu) |
|---|---|---|---|
| Baffle Type | Natural Gas | 25 (77) | 34 (0.078) |
| | Medium-Btu Gas | 49 (120) | 22 (0.051) |
| | Medium-Btu Gas | 427 (800) | 16 (0.037) |
| | Low-Btu Gas | 49 (120) | 11 (0.025) |
| | Low-Btu Gas | 427 (800) | 15 (0.035) |
| Kiln Type | Natural Gas | 25 (77) | 21 (0.049) |
| | Medium-Btu Gas | 49 (120) | 18 (0.043) |
| | Medium-Btu Gas | 427 (800) | 13 (0.030) |
| | Low-Btu Gas | 49 (120) | 17 (0.039) |
| | Low-Btu Gas | 427 (800) | 13 (0.030) |

[a] Approximate input heat rate of 1 $MW_T$ ($3.5 \times 10^6$ Btu/hr) with 10 percent excess air.

[b] NO plus $NO_x$ (dry, corrected to 0 percent excess air).

Source: Reference 61.

## TABLE 8-4. SUMMARY OF TEST DATA FOR BAFFLE BURNER

| Fuel Type | Inputs |  |  |  |  | Flue-Gas Composition (as measured) |  |  |  |  |  |  | Particulate, |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Rate $m^3/s$ | $NH_3$ % | $H_2S$ | Tar g/s | Char | NO | $NO_2$ ppm | CO | $CO_2$ % | $O_2$ | $SO_2$ | HC ppm | $g/m^3$ | g/s |
| Natural Gas | 0.027 | 0 | 0 | 0 | 0 | 112 | 10 | 10 | 10.9 | 1.9 | -- | -- |  |  |
| WGO[a] (322K, 10%) Excess Air | 0.111 | 0 | 0 | 0 | 0 | 38 | 10 | 200 | 24.0 | 1.8 | -- | -- |  |  |
| WGO[a] (700K, 10%) Excess Air | 0.140 | 0 | 0 | 0 | 0 | 30 | 5 | 115 | 24.0 | 1.8 | -- | -- |  |  |
|  | 0.134 | 0.19 | 0 | 0 | 0 | 310 | 10 | 55 | 24.0 | 1.9 | -- | -- |  |  |
|  | 0.134 | 0.38 | 0 | 0 | 0 | 360 | 10 | 55 | 24.0 | 1.8 | -- | -- |  |  |
|  | 0.134 | 0.60 | 0 | 0 | 0 | 400 | 15 | 53 | 24.0 | 1.9 | -- | -- |  |  |
|  | 0.134 | 0.81 | 0 | 0 | 0 | 420 | 20 | 55 | 24.0 | 1.9 | -- | -- |  |  |
|  | 0.134 | 1.03 | 0 | 0 | 0 | 430 | 20 | 60 | 24.0 | 1.9 | -- | -- |  |  |
| WGO[a] (700K, 20%) Excess Air | 0.134 | 0 | 0 | 0 | 0 | 38 | 5 | 45 | 22.0 | 3.3 | -- | -- |  |  |
|  | 0.134 | 0.19 | 0 | 0 | 0 | 290 | 10 | 45 | 22.0 | 3.3 | -- | -- |  |  |
|  | 0.134 | 0.38 | 0 | 0 | 0 | 355 | 10 | 45 | 22.0 | 3.2 | -- | -- |  |  |
|  | 0.134 | 0.60 | 0 | 0 | 0 | 410 | 20 | 40 | 22.0 | 3.2 | -- | -- |  |  |
|  | 0.134 | 0.81 | 0 | 0 | 0 | 435 | 20 | 40 | 22.0 | 3.2 | -- | -- |  |  |
|  | 0.134 | 1.03 | 0 | 0 | 0 | 465 | 20 | 40 | 22.0 | 3.3 | -- | -- |  |  |
| WGO[a] (700K, 10%) Excess Air Tar Doping | 0.141 | 0 | 0 | 0.36 | 0 | 52 | 7 | 108 | 24.0 | 1.8 | 1 | <1 |  |  |
|  | 0.141 | 0 | 0 | 0.50 | 0 | 55 | 5 | 93 | 24.0 | 1.9 | 1 | <1 |  |  |
|  | 0.141 | 0 | 0 | 0.71 | 0 | 58 | 4 | 93 | 24.0 | 1.9 | 2 | <1 |  |  |
| WGO[a] (700K, 10%) Char Doping | 0.138 | 0 | 0 | 0 | 0.13 | 30 | 3 | 59 | 24.0 | 1.8 | 4 | <1 | 0.037 | 0.009 |
|  | 0.138 | 0 | 0 | 0 | 0.24 | 33 | 2 | 100 | 24.0 | 1.7 | 6 | <1 | 0.070 | 0.017 |
|  | 0.138 | 0 | 0 | 0 | 0.86 | 44 | 4 | 90 | 24.0 | 1.9 | 29 | <1 | 0.263 | 0.064 |
| WGO[a] (700K, 10%) Ammonia/Tar | 0.139 | 0.99 | 0 | 0.39 | 0 | 520 | 10 | 108 | 24.0 | 1.7 | 2 | <1 |  |  |
| WGO[a] (700K, 10%) Ammonia/Char | 0.138 | 1.00 | 0 | 0 | 0.13 | 470 | 43 | 65 | 24.0 | 1.8 | 4 | <1 |  |  |
| WGO[a] (700K, 10%) Char/Tar | 0.138 | 0 | 0 | 0.46 | 0.13 | 40 | 8 | 63 | 24.0 | 1.9 | 7 | <1 |  |  |
| WGO[a] (700K, 10%) Ammonia/Char/Tar | 0.138 | 1.00 | 0 | 0.47 | 0.13 | 500 | 42 | 75 | 24.0 | 1.8 | 8 | <1 |  |  |
|  | 0.136 | 1.02 | 0 | 0.38 | 0.07 | 510 | 15 | 24 | 24.0 | 1.9 | 7 | <1 | 0.026 | 0.006 |
| WGO[a] + 15% FGR (700K, 10%) Ammonia/Char/Tar | 0.138 | 1.00 | 0 | 1.22 | 0.13 | 510 | 20 | 45 | 24.0 | 1.9 | 4 | <1 |  |  |

(Continued)

## TABLE 8-4. SUMMARY OF TEST DATA FOR BAFFLE BURNER (CONTINUED)

| Fuel Type | Inputs | | | | | Flue-Gas Composition (as measured) | | | | | | | Particulate, | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Rate | $NH_3$ | $H_2S$ | Tar | Char | NO | $NO_2$ | CO | $CO_2$ | $O_2$ | $SO_2$ | HC | $g/m^3$ | g/s |
| | $m^3/s$ | % | | g/s | | ppm | | | % | | ppm | | | |
| WGO[a] (700K, 10%) Hydrogen Sulfide | 0.134 | 1.04 | 0.02 | 0 | 0 | 480 | 29 | 40 | 24.0 | 1.8 | 83 | -- | | |
| | 0.134 | 1.04 | 0.52 | 0 | 0 | 655 | 33 | 50 | 24.0 | 1.8 | 2546 | -- | | |
| | 0.136 | 1.02 | 2.53 | 0 | 0 | 950 | 50 | 37 | 24.0 | 1.9 | 11146 | -- | | |
| WGA[b] (322K, 10%) Excess Air | 0.175 | 0 | 0 | 0 | 0 | 16 | 1 | 260 | 18.4 | 1.3 | -- | -- | | |
| WGA[c] (616K, 10%) Excess Air | 0.175 | 0 | 0 | 0 | 0 | 22 | 2 | 35 | 18.4 | 1.4 | -- | -- | | |
| WGA[c] (616K, 10%) Ammonia/Char/Tar | 0.186 | 1.04 | 0 | 0.58 | 0.35 | 610 | 20 | 40 | 18.4 | 1.4 | 8 | <1 | 0.044 | 0.016 |

[a] Wellman-Galusha oxygen fuel gas (medium-Btu gas).

[b] Wellman-Galusha air fuel gas (low-Btu gas).

[c] Wellman-Galusha air fuel gas. Uses 3-inch nozzle. (All others used 2-1/2 inch nozzle.)

gas. The thermal $NO_x$ emissions in this table are based on the IGT studies discussed above.

Table 8-5 results show that the total $NO_x$ emissions from combustion of entrained-bed gasifer product gases are projected in all cases to meet the industrial boiler limit of 0.7 lb $NO_x/10^6$ Btu and the utility boiler limit of 0.5 lb $NO_x/10^6$ Btu. These projections are based on limited (i.e., 35 to 55 percent) conversion of $NH_3$ to $NO_x$ as discussed above. If $NH_3$ conversions are higher, fuel $NO_x$ emissions will be higher and the emission limits, especially the utility boiler standard, may be exceeded. Total $NO_x$ emissions are lower for low-Btu product gases than for medium-Btu product gases primarily due to the thermal $NO_x$ contribution.

While the results in Table 8-5 indicate that boiler $NO_x$ emission standards can be met without additional control techniques, an added margin of safety would be supplied by the reduction of HCN and $NH_3$ concentrations in the fuel gas by addition of CaO or other sorbents to the entrained-bed gasifier. The extent of this reduction is not known at the present time but TRW[63,64] tests suggest $SO_x$ reductions on the order of 40 to 60 percent. Fuel-related $NO_x$ reductions of the same order or magnitude would not be unreasonable to expect. This additional $NO_x$ reduction would be most attractive in the case of 300 Btu/scf product gas being combusted in a utility boiler since emissions are very near the limit.

### 8.3.3 Sulfur Cleanup Requirements

As noted in Section 7.2.2, the sulfur species from an oxygen-blown entrained-bed gasifier are expected to range from 1.2 to 2.2 mole percent. This corresponds approximately to 7.0 to 12.6 lb $SO_2$/million Btu coal for oxygen-blown gasifier operation. For air-blown operation, uncontrolled $SO_2$ emissions would be about 5.5 to 9.9 lb $SO_2$/million Btu coal owing to the lower conversion efficiency of coal Btus to gas Btus. These sulfur and $SO_2$ values assume no in-process control in the gasifier. If this product gas is combusted in an industrial boiler, the current emission limit is 1.2 lb $SO_2$/million Btu. Thus at the higher end of the expected sulfur range for an

TABLE 8-5. ESTIMATION OF NO$_x$ EMISSIONS FROM BOILERS

| Fuel | Heating Values Btu/scf | Gas Production Rate scf/lb Coal | Fuel Related NO$_x$[e] lb/$10^6$ Btu | Thermal NO$_x$ lb/$10^6$ Btu | Total NO$_x$ lb/$10^6$ Btu |
|---|---|---|---|---|---|
| Natural Gas | 1,025 | NA | 0.0 | 0.078[a] | 0.078 |
| Med-Btu Gas | 300 | 40.5[b] | 0.22-0.31 | 0.185[d] | 0.405-0.495 |
| Med-Btu Gas | 202-267 | 60[c] | 0.23-0.32[c,f] | 0.037-0.051[a] | 0.267-0.371 |
| Low-Btu Gas | 110-159 | 86.7[b] | 0.24-0.30[f] | 0.020-0.028 | 0.260-0.328 |

NA = not applicable.

[a] Reference 6.

[b] Reference 44.

[c] Estimated.

[d] Estimated from Figure 7-2.

[e] Btu heat input based on coal feed to gasifier, except for natural gas.

[f] Based on Table 2-5 and Figure 8-4.

$O_2$-blown gasifier, 90.5 percent of the sulfur species must be removed either prior to combustion or after combustion, using the options discussed in Section 8.2.3. For an air-blown gasifier, 87.9 percent $SO_2$ removal would be required at the high end. The use of in-process control via CaO injection or the application of other sorbents is anticipated to remove up to 40 to 60 percent of the sulfur species in the gas stream based on results reported by TRW.[63,64] Assuming a middle value of 50 percent for in-process control implies that additional sulfur cleanup equipment would still be required but the sulfur removal burden, based on the remaining sulfur values, would be lowered to 81.0 percent for $O_2$ operation and 75.8 percent for air operation. This lower removal burden will reduce the size and cost of downstream equipment used for $SO_2$ control.

For utility boiler combustion of the gasifier product gas, the $SO_2$ reduction requirement will be a function of the sulfur content and heating value of the coal fed to the gasifier. The data in Table 2-5 apply to gasification of medium- to high-sulfur bituminous coals. For example purposes, assume the coal being gasified is a bituminous coal with 3.5 weight percent sulfur and 12,000 Btu/lb heating value. This corresponds to 5.83 lb/million Btu of potential $SO_2$ emissions. In this case the current utility boiler NSPS would require 89.7 percent $SO_2$ removal in order to meet an emission limit of 0.6 lb $SO_2$/million Btu. This percent reduction requirement would apply irrespective of whether the gasifier is operated in the $O_2$ or air-blown mode. With no in-process sulfur control, and assuming all the coal sulfur reports to the product gas, this $SO_2$ reduction would be required either prior to or after combustion. If in-process sulfur control techniques reduce $SO_2$ precursors by 50 percent as discussed above, the boiler sulfur reduction burden would be lowered to 79.3 percent of the sulfur values remaining in the product gas (i.e., 2.92 lb/million Btu). As in the industrial boiler case, the effect of gasifier in-process sulfur control is to reduce the size and cost of downstream equipment.

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